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UNIVERSITY OF ALBERTA

TREATMENT OF WASTEWATER FROM A KRAFT PROCESS PULP MILL USING OZONE

BY

ABDUL NAYEEM MOHAMMED

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

IN

ENVIRONMENTAL ENGINEERING

DEPARTMENT OF CIVIL ENGINEERING

EDMONTON, ALBERTA

FALL 1990

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled TREATMENT OF WASTEWATER FROM A KRAFT PROCESS PULP MILL USING OZONE submitted by ABDUL NAYEEM MOHAMMED in partial fulfilment of the requirements for the degree of MASTER OF SCIENCE in ENVIRONMENTAL ENGINEERING.

Daniel W. Smith

DANIEL W. SMITH (SUPERVISOR)

G.R. Finch

GORDON R. FINCH

John Fedde

JOHN FEDDES

Date Sep. 21 1990

To my son
Zubair

ABSTRACT

Experiments were conducted in a batch reactor for ozone doses between 50 and 200 mg O_3/L to identify the relative suitability of ozone application locations in the treatment process and see the improvements in biotreatability of wastewaters from a kraft process pulp mill. The studies were divided into three major sections: characterization of mill effluent; ozone system calibration and reactor design; and ozonation of mill effluent. Seed for Biochemical Oxygen Demand tests were acclimatized in batch units for primary, bleach and secondary effluents seperately. The inhibitory effects which were noted with unacclimatized seed, were reduced by using laboratory acclimatized seed and optimum dilution which were determined during the characterization phase.

The batch reactor designed for the studies, consisted of a cylindrical section for holding effluent, and a top spherical section for ozone / oxygen mixture. The reactor proved to be effective for controlling ozone dose. The variation in the desired ozone dose was less than 5 mg/L.

Bleach and primary effluents were treated with 50 and 100 mg/L ozone doses. Duplicate experiments were conducted for these effluents. Secondary effluent was studied for 50, 100, 150 and 200 mg/L ozone doses. Six replicate experiments were conducted for 50 and 100 mg/L ozone doses, whereas two experiments were carried out for 150

mg/L and one experiment for 200 mg/L ozone dose was performed, for investigating the effects of ozone on effluent characteristics.

The results were analyzed using 't' test for paired experiments and ANOVA table for statistical confirmation. Residuals were plotted to check the assumptions of constant variance and normanl distribution. The results indicated that 50 and 100 mg O_3/L effectively removed colour from bleach effluent and primary effluent, but did not significantly change BOD. Ozone was found to be effective for secondary effluent, as BOD_5 was increased by 65% and 100% for 50 and 100 mg O_3/L doses, respectively. The corresponding reduction in colour was 62% and 82%. K_e and L_o values for all test conditions were calculated using a computer programme for the the BOD equation, giving joint confidence regions for the calculated parameters. It was concluded that ozone is most effective for the removal of colour and the improvement of BOD in secondary effluent.

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Abbreviations

AC/MC	= Activated carbon / microcoulometric method
ADI	= Acceptable daily intake
ADT	= Air Dry Tonne
AOX	= Absorbable Organic Halides
APHA	= American Public Health Association
ATU	= Allylthiourea
AWWA	= American Water Works Association
BOD	= Biochemical Oxygen Demand
BOD_5	= 5-day Biochemical Oxygen Demand
BOD_u	= Ultimate Biochemical Oxygen Demand
C_A	= Concentration of A
C_{Ao}	= Initial concentration of A
CaO	= Lime
C_B	= Concentration of B
C_{Bo}	= Initial concentration of B
CEPA	= Canadian Environmental Protection Act
Cl_2	= Chlorine
ClO_2	= Chlorine dioxide
CMP	= Chemi-Mechanical Pulping
CO_3	= Ozone concentration
COD	= Chemical Oxygen Demand
C_T	= Total concentration
CTMP	= Chemi-Thermo-Mechanical Pulping
C_{To}	= Total initial concentration

do	= Change in dissolved oxygen concentration
dt	= Change in time
f_o	= Total colour in the effluent
GAC	= Granular activated carbon
H_2SO_4	= Sulfuric acid
HCl	= Hydrochloric acid
$HgSO_4$	= Mercuric sulfate
HNO_3	= Nitric acid
Ho	= Null hypothesis
k_1	= Synthesis energy rate constant
K_A	= Reaction rate constant for A
K_B	= Reaction rate constant for B
K_e	= Rate constant in BOD equation (biodegradibility constant)
k_e	= Endogenous rate constant
k_{er}	= Endogenous removal rate constant
KHP	= Potassium hydrogen phthalate
k_r	= Substrate removal rate
Kwh	= Kilowatt-hr
LC_{50}	= Lethal Concentration which would kill 50% of test fish
min	= minutes
MISA	= Municipal Industrial Strategy for Abatement Program
mL	= millilitre

mm	= millimetre
MST	= Mean Survival Time
N	= Normality
n	= Number of data points
Na_2CO_3	= Sodium carbonate
Na_2S	= Sodium sulfite
NaCl	= Sodium chloride
$NaClO_3$	= Sodium chlorate
NaOCl	= Sodium hypochlorite
NaOH	= Sodium hydroxide
NCASI	= National Council of the Paper Industry for Air and Stream Improvement
NDIR	= Non-dispertive infra-red detector
O_2	= Oxygen
O_3	= Ozone
P_a	= Barometric pressure
PAC	= Powdered Activated Carbon
PCDD	= Polychlorinated dibenzo-p-dioxins
PCDF	= Polychlorinated dibenzo-furans
P_m	= Corrected pressure
ppt	= Parts per trillion
P_s	= Standard pressure mm Hg
PVC	= Polyvinyl chloride
P_w	= Vapour pressure of water at 20° C
R_a	= Ozone monitor constant

S	= Substrate concentration
S^2	= Variance
SCMP	= Semi-Chemi-Mechanical Pulping
S_o	= Initial substrate concentration
SO_2	= Sulfur dioxide
SS	= Suspended Solids
STP	= Standard temperature and pressure
t	= time
T4CDD	= Tetrachloro dibenzo-p-dioxin
T_a	= Room temperature K
TCDF	= Tetrachloro dibenzo-furan
TKN	= Total kjeldahl nitrogen
TMP	= Thermo-Mechanical Pulping
TOC	= Total Organic Carbon
TOX	= Total Organic Halides
T_s	= Standard temperature K
TSS	= Total Suspended Solids
US EPA	= United States Environmental Protection Agency
UV	= Ultra violet
V_m	= measured gas flow rate
V_s	= Corrected gas flow rate
VSS	= Volatile Suspended Solids
WPCF	= Water Pollution Control Federation
X_a	= Active mass concentration
X_{ao}	= Initial active mass concentration

°C = Degree centigrade

°K = Degree Kelvin

1.0 INTRODUCTION

1.1 Background

Pulp and paper is one of the largest industries in North America and plays a vital role in the economy of Canada. Canada is a world leader in the export of newsprint pulp. The importance of the pulp and paper industry is primarily due to the abundance of forest available for pulping.

Pulp mill operation has been an important but relatively small industrial component in Alberta for several years. Before the recent attempts to diversify the provincial economic base, Alberta was producing about 2% of the total Canadian pulp. However, with five new mills planned or under construction and three more being considered, the pulp and paper industry is going to have a significant effect on the provincial economy and the receiving environment. The new mills will be located in northern Alberta drainage basins discharging their treated wastewater into the Peace and Athabasca River systems (Figure 1). The capacity of the river systems to assimilate the residual biodegradable organics has become an important issue.

A recent environmental impact study done by Alberta Environment on Athabasca River due to the existing mill discharges indicated that during low flow winter conditions there were situations where the river oxygen is depleted to critical levels with the existing mills itself.

Figure 1. New and Existing Pulp Mills in Alberta (Adapted from Edmonton Journal, 1989)

The recent expansion of the industry will create thousands of direct and indirect jobs injecting about $3.2 billion into Alberta economy. However, the public is concerned about the environmental impact of the new mills on the water quality of the rivers. Especially since all but one of the proposed mills will incorporate a Kraft process for pulping and chlorine bleaching (partly) operations, which are known to produce organochlorines and dioxins. The Kraft process with chlorine bleaching is the choice of most mills because it is a proven technology for best quality pulp.

Currently government agencies are trying to balance the economic development that the proposed mills represent with concerns for the environment.

As a result the environmental protection agencies are attempting to evolve more stringent regulations to make sure that the environment is protected adequately without unduly effecting the economic developments. They also have drafted a rational program such that the pollutants levels could be achieved over a reasonable period of time.

The treatment methods practiced in the pulp and paper industry are: aerated lagoons; anaerobic treatment; and activated sludge processes. Aerated lagoons are most commonly used for treating mill effluent in Canada. Aerated lagoons are well suited for the removal of soluble forms of BOD exerted by simple compounds to the extent of 80 to 90%. However their effectiveness is limited for the removal of colour, foaming and odorous compounds, complex forms of BOD and organic halides (Bauman et al., 1974; Chen et al., 1974; Bryant et al., 1987). As a result when discharged, these compounds impact the receiving environment.

Presently Canada has no guidelines for the discharge of colour and other pollutants except for the BOD and chloroorganics. However, COD, colour and foaming compounds effect the receiving water directly, and are responsible for inefficient removal of pollutants during the external treatment process.

Ozone, being a strong oxidizing agent, next to fluoride, has been used at bench and pilot levels for the treatment of pulp mill effluent. Previous studies have invariably indicated the effectiveness of ozone for the removal of colour, odour and improvements in treatability of

pulp mill effluent but the effect on BOD has been reported to vary depending on the strength of the effluent. For high initial BOD, ozonation results in a decrease of BOD of the treated effluent, whereas, for low initial BOD, there is an increase in biochemical oxygen demand after ozonation.

Pulp and paper mill effluent has always been associated with complex forms of COD which is hardly effected during the conventional treatment processes. The organics discharged into the river, thus persist in the environment for a long time and act as precursor for the formation of undesirable compounds when the water is treated for domestic use.

Presently ozone is an expensive treatment option but with the growing public concerns towards the environment and greater necessity for recycling the effluent, it is an attractive treatment. With the improvement in ozone generation methods, cheaper power, and more effective means of ozone application, ozonation is an attractive technology for the treatment of pulp mill effluent. Ozone application is further justified with changing regulations and more stringent guidelines being continuously revised by the regulatory bodies.

Ozone treatment is an effective alternative for removal of colour, odour and foaming characteristics, and for the improvement of overall treatability of pulp mill effluents. The advantages of ozonation are:

1. the process is simple and compatible with existing treatment systems;

2. it can be incorporated as a pre- or post-treatment in existing systems without major modifications;
3. ozone treatment does not produce by-products to be handled separately as in case of coagulation and lime treatment for colour removal;
4. being a strong oxidizing agent, ozone reacts with various compounds removing colour, foaming characteristics and odour, while breaking larger molecules into smaller fragments making them more easily biodegradable; and
5. after ozonation the effluent has a high level of dissolved oxygen. If oxygen is used to generate ozone, the dissolved oxygen can be as high as 30 to 40 mg/L, depending on its temperature.

The disadvantages of ozone are:

1. very high ozone demand for the treatment of wastewater;
2. fluctuations in ozone demand with the variations in effluent quality, which would make the sizing of the ozone generation system difficult; and
3. higher capital and operational cost for ozonation system.

However, the first two disadvantages can be controlled by selecting a suitable location of ozone application such that the effect of quality variation is minimized, and designing a good ozone contact system to improve the efficiency of ozone utilization. Operational cost can be minimized by improved ozone generation system. For pulp mills, it has been reported by Nebel et al. (1974) that due to lagging power factor in the mill, installation of ozone system would improve

the overall power factor, thus improving the efficiency of power utilization.

All the above mentioned attractive features make ozone a potential alternative to enhance the overall treatability of the pulp mill effluent.

1.2 Scope of Study

The study was planned to see the effect of ozonation on kraft process pulp mill effluent. The research was divided into five steps which were as follows:

1. characterization of pulp mill effluent ;
2. evaluation of the effect of ozone on BOD of primary, bleach and secondary effluent;
3. colour removal for mill effluents;
4. effect of ozone on COD,TOC (filtered and unfiltered), and suspended solids (total and volatile); and
5. identification of relative suitability of ozone application location in the treatment process.

2.0 LITERATURE REVIEW

2.1 Environmental Guidelines

To establish a balance between economic development and environment protection, the environmental protection agencies are attempting to evolve more stringent effluent discharge guidelines. The industry is in a constant search for the development of technologies which would reduce the environmental impact , at the same time produce reasonably good quality pulp.

Presently the US EPA is focussing attention on toxic substances in pulp mill effluent. It is expected that effluent limitations will be set for 65 specific compounds identified from pulp, paper and paper board mill effluents.

Under the Canadian Environmental Protection Act (CEPA) which was proclaimed on June 30, 1988 and designed to take preventive approach for the protection of the environments, regulations are being developed to control the discharge of dioxins and furans. The other steps taken under CEPA are to assess the mills using bleaching operations and determine what substances in addition to dioxins and furans should be controlled in the mill discharge (Halliburton and Ruthman ,1989). It is expected that regulations to control dioxins and furans could be promulgated under CEPA by the middle of 1990 (Halliburton and Ruthman, 1989).

Ontario has taken steps in the direction of developing strict guidelines for mill discharges and achieving the goals over an

acceptable period of time in consultation with the industry under the Municipal Industrial Strategy for Abatement Program (MISA). Under the interim strategy, mills are expected to achieve the quantities of absorbable organic halides (AOX), BOD_5 and suspended solids discharged in the mill effluent, to level IV by 1993 (Table 1, Turner 1989). The present levels of AOX discharges range between 1 to 5 kg AOX/ADT (i.e. air dry tonne). These levels are expected to be achieved by modifying the pulping and bleaching techniques. A survey of the mills in Ontario indicated that mills that are discharging AOX below 2.5 kg/ADT are practicing oxygen delignification and high chlorine dioxide substitution (Turner 1989).

Table 1. Level of achievement for kraft process pulp and paper mill effluent (Adapted from Turner, 1989).

Level	BOD (kg/ADt)	Suspended solids (kg/ADt)	DO in receiving water	Lethality of effluent for discharge volume of 175 m3/t	Sublethal toxic effect beyond the mixing zone	Organochlorines kg TOX/ADt
I	>30	>15	DO at low level	LC50< 50%	Yes	≥5.0
II	<30/16.5	<15	DO meets low level	LC50> 50%	Yes	<4.5
III	<30/16.5	<10	DO meets moderate level	LC50≥100%	None	<2.5
IV	<30/16.5	<10	DO meets high level of protection	LC50≥100%	None	<1.5

A similar approach has been adopted by Alberta Environment for reducing discharge of AOX/TOX (total organic halides) and biodegradable organics in the mill effluent. A number of studies have been conducted to determine the ultimate BOD of the mill effluent. Also river modeling under summer and winter conditions have been conducted to study the effects of mill discharges. The results of these studies are very interesting and it is expected that in the future all the mills would be required to monitor long term BOD of the mill discharges.

The solution to the problem lies in the pulping and bleaching operations controlling the quality of mill effluent. The pulping and bleaching operations practiced in the industry are briefly described in the following section.

2.2 Pulping Processes

The objective of pulping operation is to separate the fibres by dissolving lignin. The degree of degradation of wood during the process controls the yield of the pulp and effluent characteristics.

Pulping is done by various methods depending upon the type of wood and quality of the pulp requirements. The methods used in the industry are described below.

2.2.1 Chemical Pulping

1. alkaline cooking known as kraft process uses sodium hydroxide and sodium sulfite for the separation of fibres from lignin;
2. acidic process or sulfite process uses H_2SO_3 and bisulfite.

2.2.2 Semi-Chemical Pulping

In this process, wood is cooked for a limited time period to achieve partial delignification, thus improving the pulp yield and reducing the degradation of cellulose during the pulping process.

2.2.3 Mechanical Pulping

This was basically developed to minimize the water use and reduce the effluent quantity. This method requires higher energy for the pulping operation.

2.2.4 Thermo-Mechanical Pulping (TMP)

This process is an improvement to mechanical pulping and requires lesser energy for pulping the wood. In the TMP process, wood is steamed for a short period of time prior to and during pulping process. Steam serves to soften the wood chips and makes the pulping process more energy efficient. TMP process has the advantages of higher pulp yield (91 to 95%) and improved quality of mill effluent.

2.2.5 Chemi-Mechanical Pulping (CMP)

This process requires chemical pre-treatment of wood chips at temperature below 100° C.

2.2.6 Semi-Chemi-Mechanical Pulping (SCMP)

Chemicals are added to the wood chips prior to or during pre-steaming at temperature above 100° C. Chemicals dose depend on the quality of wood.

2.2.7 Chemi-Thermo Mechanical Pulping (CTMP)

In this process, the pulping chemicals are added to the wood chips prior to or during pre-steaming at temperature above 100° C. The typical yield is between 80 to 90%.

2.2.8 Commonly Used Pulping Methods

Pulping operations play an important role in the quality and quantity of the effluent. The two most commonly used techniques from the above list are the kraft process and the thermo mechanical pulping (TMP) process. The modified versions of these two process are used depending on the type of wood available as raw material and the quality of the pulp required.

The Kraft process, in which pulping is based on dissolving the binding substance, i.e. the lignin and separating long intact and strong fibre gives a superior quality pulp. However, the pulp yield is limited to a maximum of 55%. Water consumption in this process is of the order of 75 m^3 /tonne of finished product; it yields dark coloured pulp which is bleached for further use.

Thermo-mechanical pulping process requires wood to be steam treated making it softer and then separates the fibres by mechanical means. The TMP process does not remove lignin from the wood and requires less bleaching. The TMP process is receiving a wide acceptance in the industry and produces pulp of reasonably good quality to be used for various kinds of finished products. Another advantage is the lower water consumption which is of the order of 27 m^3/tonne.

Unlike the kraft process where bleaching is done to remove lignin; mechanical pulp is bleached with the objective of oxidizing the lignin without its removal. This fact significantly reduces the bleaching load and more expensive, but environmentally sound methods of bleaching can be applied.

2.3 Bleaching Operation

Chemical pulp, which is dark in colour requires bleaching before further use. About 70% of the kraft process pulp and 20% of sulfite pulp produced in Canada are bleached using the conventional techniques (EPS 1984).

The conventional bleaching process using chlorine produces one half the BOD, most of the effluent toxicity and colour in the mill effluent (EPS 1984). Traditional bleaching process causes about 7% of the weight of the pulp discharged to the sewer in the form of a wide variety of compounds including organochlorines (Bonsor et al. 1988).

Prior to 1970, kraft process pulping plants were based on chlorine and chlorine compounds bleaching. Since 1970 oxygen has partially been used for bleaching operations. The principal reasons for substituting other chemicals for chlorine in bleaching systems are to reduce chemical costs and improve the quality of the mill effluent.

The other alternatives to improve the quality of bleached effluent are the application of various combinations of chlorine, chlorine dioxide, oxygen, hydrogen peroxide and ozone in the bleaching operations with the objectives of reducing toxicity, TOX, AOX and BOD in the mill effluent.

It is a common practice for the mills to substitute 5 to 15% of chlorine dioxide in the first stage of the bleaching plant (Bonsor et al. 1988). Up to 70% chlorine dioxide can be substituted in the bleaching operation. Substitution of chlorine dioxide up to 50% has little impact on chemical costs, but higher levels can increase the cost markedly (Bonsor et al. 1988).

The main advantage of chlorine dioxide substitution is the reduction in AOX and TOX in the mill effluent. Higher chlorine dioxide substitution may not improve the acute toxicity of the mill effluent but the total production of toxicants is reduced substantially. Another benefit of chlorine dioxide substitution is the drop in mutagenicity of the mill effluent. A substitution of 100% chlorine dioxide for bleaching operation drops the mutagenicity of the effluent to no higher than in the control tests (Bonsor et al. 1988).

Chlorine dioxide is an unstable compound, therefore mills prepare it on site using sodium chlorate and sulphur dioxide or methanol as reducing agent. The capital cost of using chlorine dioxide generating capacity varies from $100,000 to $200, 000 per daily tonne of additional chlorine dioxide required (Bonsor et al. 1988).

Oxygen delignification or bleaching is the most promising step towards the reduction of chloro-organics and BOD discharges of mill effluent. Oxygen delignification can be used to reduce the Kappa number (measure of the contents of ligneous and related organic material) of the kraft pulp by about 50% which results in reduction of about 40% in the quantity of chloro-organics generated in the

subsequent bleaching operations (Bonsor et al. 1988). The substances removed from the wood during oxygen delignification can be recycled to the chemical recovery system, thus permitting incineration of the organics which otherwise add to BOD, organo-chlorines, toxicity and colour in the bleach plant effluent. The installation of oxygen delignification can reduce the BOD discharges by 50% and colour by 60% (McCubbin et al. 1983). Discharge of chloro-organics can be reduced by 35 to 50% (Norstrom 1987). The other advantages which has been reported are reduction in toxicity and mutagenicity. Arhippainen and Malinen (1987) claimed 50 % reduction in amount of toxicity (i.e. toxic units per tonne of pulp). A reduction of 50 to 70% in acute toxicity to fish have been reported by Idner (1987). Germgard et al. (1985) reported reduction in mutagenicity of chlorinated effluent from a response level of 600 to levels of 20 to 40 with oxygen delignification.

The concerns raised by the mills to adopt oxygen delignification technology are:

1) pulp quality is inadequate for market grade mills; and

2) brightness stability of the finished product.

However, oxygen delignified pulp is claimed to suffer less brightness reversion than traditionally processed pulp. At the same time the strength of the oxygen delignified pulp has been reported to be comparable to traditional kraft process pulp (Tench and Harper 1987, Bonsor et al. 1988).

The other doubts raised by the mills are, oxygen delignification system is difficult to operate, requires higher operational control, capital cost may be excessive, oxygen is hazardous and future chemicals cost are unknown. Bonsor et al. (1988) analysed the above concerns based on the literature and on hand experience available with the industry and concluded that the benefits of introducing oxygen delignification in the process are much more in comparison to the technical concerns that can be resolved with improved process control techniques.

The other methods of bleaching the pulp, use hydrogen peroxide/oxygen, hydrogen peroxide/ozone, and hydrogen peroxide/oxygen/ozone. These processes of bleaching are effective but costly, therefore they are not used for bleaching kraft process pulp which requires high degree of bleaching. Hydrogen peroxide bleaching can be used for thermo-mechanical process pulp (TMP) where the degree of bleaching required is less.

In a kraft process pulp mill with a chlorine based bleaching process, chlorinated organics can be reduced by using oxygen delignification and partial substitution of chlorine dioxide. Other ways to control chlorinated organics are effective washing and screening operations before the bleaching operation. The residual lignin and other compounds, which are not removed from the pulp, react with chlorine, causing higher chlorine consumption as well as generation of chlorinated compounds which are more objectionable in the mill effluent.

2.4 Problems with Mill Effluent

Pollution problems associated with pulp and paper mill effluents are complex and vary in nature; the reasons being the various processes employed for the manufacture of different grades of paper and other finished products which require varying degree of bleaching. The raw materials used and the in-plant techniques adopted for reducing process water requirements also effect the quality of the mill effluent significantly. As a result, as much as 100% variations in quality and quantity of effluent are very common.

The other dimension of waste management is the large volumes of effluent produced in the mill. In 1970, the average bleach kraft mill in Ontario discharged about 250 m^3/tonne pulp. However, since that time a number of in-plant measures have been adopted to reduce the quantity of process water and, 120 m^3 /tonne, effluent was discharged in 1986 (Bonsor et al. 1988).

2.5 Pollutants in Pulp Mill Effluent

The compounds in the mill effluent which may have deleterious effects on river characteristics are:

1. toxic compounds (TOX, AOX, resin acids etc.);
2. suspended solids;
3. BOD;
4. COD;
5. taste and odour causing materials;
6. colour causing materials;

7. pH; and

8. foaming and surface active compounds.

Although the above listed parameters are common for all the wastewaters, their concentration, degree of complexity, difficulty of treatment and damage to the receiving environment varies greatly for different sources of wastewater.

2.5.1. Toxic compounds

In a kraft mill effluent, many of the toxic compounds can be broadly classified as organochlorines which are a wide variety of chlorinated compounds. About 300 low molecular weight organochlorines have been identified in bleach plant waste which represent under 10% of the total weight (McKague 1988 and Bonsor et al. 1988). Chlorinated phenolics, chlorinated resins and fatty acids account for much of the acute toxicity of bleach plant effluent. Most of them are lethal to fish at about 1 mg/L or a few mg/L (Bonsor et al. 1988). The bioaccumulation characteristics are another concern for these chlorinated organics. Low molecular weight compounds are moderately bioaccumulative but are readily excreted when the organism moves to clean water. The high molecular weight lignins are persistent for decades in the receiving environment but they are not very toxic in nature. Fish caught even 16 months after the closing of mill operation showed an accumulation of chlorinated compounds (Cook et al. 1973). Passino and Smith (1987) reported 476 organic contaminants in wild lake trout and walleye from the Great Lakes, compared to only 8 compounds in lake trout from a hatchery. Some of

these compounds were lethal to an aquatic organism at fractions of parts per million, and organochlorines were well represented.

Specific to the kraft process effluent Leach and Thakore(1975) found that the major chlorinated organics averaged 4.3 times their lethal concentration in caustic extract streams of kraft mill effluent.

Swedish research as reported by Bonsor et al. (1988) showed that the sub-lethal effects include enlarged liver, strong induction of mixed function oxidase ("defence enzymes") of the liver, strongly abnormal metabolism of carbohydrates, and drop in white blood cell counts. Some of these effects were persistent 8 to 10 km down the river where the dilution was as much as 1140 times (Bonsor et al. 1988). These effects were more pronounced near the bleached mills, but the effects on most of the physiological parameters were considerably lower near unbleached mills.

All the findings strongly suggest that the effects of toxic compounds can not be underestimated and steps should be taken to effectively reduce their production in the process as well as provide effective treatment for their subsequent removal during the external treatment.

2.5.2 Suspended Solids

The severity of the problems caused by suspended solids are due to the blanket formation on the bottom of the low flow sections of the rivers, when large quantities were discharged with the mill effluent. Large quantities of suspended solids when discharged into the receiving bodies may result in the mat formation. Their subsequent

anaerobic decomposition can result in the elimination of total benthal habitat. Soft wood fibres at a concentration of 2000 mg/L caused some mortality of fat head minnows in four days (Smith et al. 1965). However, this problem has been very well controlled with installation of primary clarifier at the treatment facilities.

The concentrations of suspended solids in the effluent varies with debarking techniques (dry or wet) as well as the other unit operations in the pulp and paper manufacturing process. Water spills in the paper manufacturing section contributes the most to the mill effluent.

Since suspended solids in the mill effluent are cellulose material, if not removed in the clarifier, the majority will pass through the lagoon. Some solids are removed by settling into the treatment lagoon and the remaining suspended solids are discharged with the treated effluent.

Another feature of suspended solids is their adsorption capacity. As a result, they may adsorb various compounds present in the mill effluent. The adsorption process may result in the transfer of toxic compounds to the benthal zone of the river, thus affecting the benthal zone community.

2.5.3 Chemical Oxygen Demand

Chemical oxygen may not be of concern for domestic waste or waste from the food processing industry where the organics are mostly biodegradable in nature. In pulp mill effluent most of the organics are complex in nature, and they cannot be simply biodegraded. Since these

compounds are not fully accounted for by the BOD test, and there is no guideline for the discharge of COD in mill effluent. Most of the complex compounds are lignin and chlorolignin origin. Part of these compounds in the mill effluent are adsorbed on the suspended solids and settle in the bottom of the river. Some of the dissolved organics may be adsorbed by the fish mass, causing tainting or other chronic disorders. Exposure to 10% combined effluent for 7 days resulted in fish tainting (Cook et al. 1973). It was believed that fish living in or near the outfall area could be tainted with the mill effluent. The bioaccumulation characteristics of some of the compounds present in the mill discharge may not be dissipated fast from the aquatic organisms. It is also believed that the relatively complex compounds which remain in the water body slowly start degrading and convert into simpler compounds, and might be more toxic to aquatic organisms than the original compounds. The dissolved organics may also act as precursor to undesirable compounds, formed during the disinfection process when the water is used for domestic supply in the downstream communities.

2.5.4 Colour

The compounds responsible for colour in the mill effluent are lignins and chlorolignins. The studies on pulp and paper mill effluent indicated that colour is hardly affected during the aerobic or anaerobic treatment processes; it rather increased after the treatment (Lee et al. 1989). These results indicate that colour causing compounds are

resistant and may remain unaffected even in the receiving water except their effect is diluted.

The primary effect of colour on the receiving water is its influence on the photosynthesis process. The colour, present in water will reduce the light penetration and as a result, the bacterial die-off rate may also be reduced. The discharge of intensely coloured industrial effluent not only effects the aesthetic quality of the receiving waters but also reduces the rate of oxygen production due to photosynthesis. The US EPA is seeking to limit the discharge of colour pollutants in the natural waters such that it cause less than 10% change in the balance of oxygen production by photosynthesis versus oxygen uptake rate by respiration. Colour substances also form complexes with metal ions. This phenomenon might increase the cost of water treatment as well as probability of contamination of water supplies with heavy metals. Some of the rivers may already have high background colour and therefore it is not desirable to allow the mills to discharge more colour into the river. The effect of colour discharged with mill effluent may be more significant during the low flow conditions.

2.5.5 Biochemical Oxygen Demand

BOD is the measure of the dissolved oxygen consumed by microorganisms as they consume the organics in the wastewater. The BOD parameter is significant with respect to design and operational aspects of a treatment facility, as well as it is used as a catch-all term for

biodegradable organic material. The commonly used BOD_5 has little significance for pulp mill effluents for the following reasons:

1. BOD is the measure of only biodegradable material, whereas the persistent and complex compounds may not be biodegradable ;
2. It is necessary to remove all kinds of toxic and inhibitive effects during the BOD measurements, otherwise the results are biased and difficult to interpret;
3. BOD_5 is about 67% of the ultimate BOD for domestic wastewater and effects of the effluent discharge from a municipal source can be anticipated. For pulp mill wastewater the ultimate BOD can be as high as 3 to 6 times of BOD_5.

In general BOD may not be a problem until the receiving bodies are over loaded with the biodegradable material. Oxygen sag in a river may be a concern if large amounts of BOD are discharged in the effluent. In an aerated lagoon, about 80% of the ultimate BOD (BOD_u) can be removed; the remaining 20% of the BOD_u in the mill effluent may be more complex in nature and exert a lower rate of oxygen demand. Oxygen depletion may be more significant if the cell mass is not removed from effluent before discharged to a river as the endogenous respiration of the microorganisms will exert oxygen demand. The problem can be even more serious if the reaeration process is not good, as during ice cover conditions. There has been

occasions in Alberta when the oxygen, in certain section of the rivers had reached critical levels.

The above problems associated with pulp mill effluent call for an effective in-plant management and external wastewater treatment approach to achieve the goals of receiving environment protection.

2.5.6 Tainting of Fish

Kraft mill effluent can cause fish tainting at concentrations in the vicinity of 1% of the water. In some cases the fish tainting thresholds are at 0.1 or 0.2 of the LC_{50}, approximately equal to the lower range of concentrations causing sublethal effects on fish (Bonsor et al. 1988). There have been field studies on the taste of fish caught in various locations, or held in cages. All the studies confirm that tainting does occur. The compounds responsible are, condensate from recovery furnace and evaporators of a Kraft process pulp mill (Cook et al. 1973).

2.5.7 Taste and Odour

Kraft mill effluent can also cause taste and odour problems at low concentrations. For pure drinking water the concentration of effluent may be as low as 1%, but for normal water it may be higher (Bonsor et al. 1988). Very pure drinking water may be impaired with as little as 0.1% to 0.4% of biologically treated effluent. For untreated effluent this concentration may be a magnitude lower (Kovacs and Voss 1986). Though secondary treatment reduces the taste and odour problem but does not eliminate it completely (Kovacs and Voss 1986).

Taste and odour are two more physical quantities of river water which are affected by the pulp mill discharge. Cook et al. (1973) studied the effects of pulp mill effluent on the taste and odour of receiving waters. The results indicated that kraft mill effluent had a definite effect upon the odour of river water which persisted for about 3 km downstream. After this section the threshold odour of the river water returned to upstream value.

Similarly sulphite mill effluent had been found to be the main source of taste imparted by the mill effluent to the river water. This taste was described as sour; the taste was also noticeable up to a distance of 3 km downstream.

2.5.8 Foaming and Surface Active Compounds

The foaming characteristics of pulp mill effluent is also responsible for toxicity as well as lower oxygen transfer rates in the receiving waters. The work done by Ng et al. (1978) on detoxification of kraft mill effluent by foam separation varifies the toxic nature of the foam fraction. Foaming can be the biggest problem for surface discharges; but mill effluent discharged through the diffusers reduce the visual effect significantly.

The foam formed on the surface of aerated lagoon has been found to be effective in retaining the heat during winter period, at the same time it can cause severe problems with biological treatment restricting the oxygen transfer rate and requiring higher capacity aerators.

2.6 External Treatment Processes

The general trend in the industry is to adopt in-plant techniques to improve the quality of the effluent. However, the effluent, even after taking various in-plant measures does not meet the regulatory standards, therefore requires external treatment to bring the pollutants to desired levels.

As a pretreatment, neutralization is achieved by using waste chemicals and appropriately mixing selected effluent streams. Lime mud and alkaline sewer are mixed to roughly adjust the pH to a final pH of (6.5 to 7.5). Adjustment can also be done by adding acid or caustic as required.

2.6.1 Primary Treatment

Primary treatment is accomplished in a gravity clarifier, consisting of a circular tank equipped with sludge removal mechanism. In general 80 to 90% removal of suspended solids is achieved in a well designed system.

2.6.2 Secondary Treatment

2.6.2.1 Aerated Lagoon

The objectives of biological treatment are to reduce the BOD of the effluent by 70 to 95% and render the effluent non-lethal to aquatic organisms. In Canada the most commonly used method of secondary treatment is the aerated lagoon with a retention time between 5 to 10 days. Aerated lagoons offers good treatment. Cheaper land availability in Canada make them more cost effective compared to other processes. The long retention time is another advantage of this system and offer

good resistant to shock loadings and quality and quantity variations (Curtis et al. 1987).

Aerated lagoons provide distinct advantages over high rate systems. Some of these advantages are:

a) ability to absorb shock loads of concentrated effluent without appreciable change in treatment efficiency;
b) little or no nutrients required except at initial start-up (hence little extra nutrient discharge to the receiving water);
c) lower net settleable solids generation, thus avoiding clarification processes and sludge disposal;
d) lower energy consumption due to avoidance of sludge handling;
e) better toxicity removal;
f) higher reliability due to the simplicity of the mechanical equipment; and
g) toxic compounds which degrade slower can be better removed due to longer retention time.

The disadvantage of the system is, performance variations with temperature and insufficient removal of suspended solids (biomass) , since most of the treatment facilities do not have a secondary clarifier.

2.6.2.2 Activated Sludge Process

This process is characterized by high concentrations of active mass which contact with the wastewater for a shorter period of time. The mixed liquor suspended solids concentration are in the range of

2000 to 5000 mg/L compared to 50 to 200 mg/L in aerated lagoon (Edde 1988). At the same time oxygen is supplied at a high rate. The organic matter present in the waste is removed both by utilization by the microorganisms and adsorption on the active mass, therefore a high degree of organic matter is removed in a shorter period of time. The excess sludge generated is removed and dewatered for disposal.

Activated sludge plants require more labour and technical expertise for operation. The additional cost may be approximately $300,000 /year for an Ontario mill (Bonsor et al. 1988). The activated sludge process can be more economical where the land required for aerated lagoon is very expensive.

2.6.2.3 Oxygen Activated Sludge Process

Chen et al. (1974) studied oxygen activated sludge, rotating biological surface, plastic medium trickling filter and aerated stabilization pond for the treatment of effluent from an integrated paper mill using bleach kraft and refiner groundwood pulping process. Oxygen activated sludge and rotating biological surface achieved about 90% BOD removal, trickling filter about 72% and aerated stabilization basin about 83% for a hydraulic retention time of 7.6 days. However, these processes did not remove colour. All the four processes were found to be susceptible to shock loadings and the recovery time following the upset was 2 to 3 days.

Fell and Reid (1987) reported UNOX oxygen-activated sludge process being effective in foam control, compared to air-activated sludge process.

2.6.2.4 Anaerobic Treatment

Anaerobic treatment for the removal of complex compounds has been reported to be effective (Lee et al. 1989). Its effectiveness with moderately strong effluent to achieve effluent BOD criterion might be questionable. A well designed anaerobic treatment system can be effective for breaking complex compounds by a well adapted population of microorganisms but the effectiveness of an anaerobic lagoon is questionable due to limited control on the process parameters. One of the problems associated with anaerobic treatment is the slower growth of micro-organisms and greater control on process parameters such as temperature, pH etc. As a result any kind of upset in the treatment system would be very difficult to control in a short period of time.

2.6.3 Physico Chemical Processes

Lime is successful in removing toxicity from some waste streams but not others (Bonsor et al. 1988). Alum or ferric chloride will make the effluent non-lethal. The above treatments may not be employed due to sludge handling problems.

2.6.4 Ozone Treatment

Ozone treatment is an effective alternative to remove colour, odour, foaming characteristics and improve overall treatability of the pulp mill effluent. The advantages of ozonation are given in the introduction.

As a strong oxidant ozone can be effective for the removal of colour, surface active compounds, odour, toxicity and improvement in

biotreatability of pulp mill effluent by breaking complex molecules which may produce compounds which are more biodegradable.

Bauman and Lutz (1974) studied the ozonation of secondary effluent from an integrated kraft mill making 500 ton/day of fully bleached pulp and 600 ton/day of fine papers using a 5 gal/min pilot plant. Application of 30 to 40 mg O_3/L reduced colour by 60 to 70%, COD by 10%, suspended solids by 22% and increased BOD_5 by 105%. The initial BOD_5 of the effluent before ozonation was 10 mg /L. The increase in BOD_5 was reported to be consistent for the replicate runs. They developed a regression equation including variables such as ozone dose, initial colour, COD, suspended solids and units of colour lost during ozonation. The regressed equation is:

$$\% \text{ colour removed} = 67.4 + 0.0552 (\text{ppm } O_3) - 0.111 (\text{COD}) - 0.068 (\text{initial colour}) + 0.159 (\text{suspended solids}) + 0.144 (\text{unit of colour lost}) \quad (1)$$

Higher ozone doses were applied to see the effect of extended ozonation on the parameters. 80% colour reduction was achieved at 80 mg O_3/L dose. Even after 300 mg/L ozone, about 30 APHA units colour was still remaining. At 40 mg/L ozone dose 99% of the coliform bacteria were killed and 99% of the total bacteria were killed at 100 mg /L ozone dose. Cost analyses indicated that for the secondary effluent with a flow rate of 7500 m^3/day, initial colour less than 1000 mg/L, COD of about 200 mg/L, suspended solids less than 50 mg/L, 500

ton/day pulp production and power cost at \$0.15/kW.hr would cost \$2.00 to \$2.75/ton of pulp to give a effluent colour in the range of 150 APHA units. Any further colour reduction would require disproportionately larger amounts of ozone.

Ng et al.(1978) carried out ozonation of a kraft mill effluent. A total of four samples were collected from two kraft process mills. Three of the samples were toxic to fish with mean survival time (MST) values ranging from 290 to 420 minutes. Colour varied from 1780 to 3000 APHA units. The BOD_5 of the samples ranged from 190 to 250 mg/L and TOC from 270 to 330 mg/L. An amount of 8.8 mg/L ozone was applied to all the samples at pH 4.2, 7.0 and 9.0. Toxicity tests were conducted using juvenile rainbow trout for all the ozonated samples and a control sample using oxygen. Detoxification was improved at higher pH, with a marginal toxicity removal at pH 4.2 and highest at pH 9.0. The improvement in toxicity removal, however could not be attributed to ozonation. The toxicity removal showed a similar pattern for various pH runs for control sample (i.e. higher toxicity removal at pH 9.0). It was noticed that during all the experimental runs foam separation occurred which might be actually responsible for reduction in toxicity. 8.8 mg/L ozone dose resulted in 10% reduction in colour, but the effect on BOD_5 or TOC was insignificant and the small variations in the parametric estimates were believed to be due to experimental errors.

Application of 50 mg O_3/L progressively reduced the toxicity and the MST values of 390 to 420 minutes were increased to 1000 minutes

for the treated samples. Similar reduction in toxicity were noticed for the control experiments with oxygen, and the toxicity removal was believed to be due to foam separation which occurred concurrently.

It was noticed that colour was readily removed by ozonation. Colour removal was highest for initial doses, declining gradually with additional applications of ozone. A logarithmic plot of the data produced a reasonable straight line suggesting that ozone requirements increase exponentially with progressive oxidation of the chromophores. The mathematical relationship developed can be given as:

$$\ln(\text{colour removed}) = 0.72 \ln(\text{ozone applied}) + 3.78 \qquad (2)$$

Application of 48 mg O_3/L reduced the effluent colour by 28 to 34% for an initial colour of 1880 to 2080 APHA units. The developed mathematical relationship suggested that about 150 to 175 mg/L ozone would have to be applied to achieve a colour reduction of 90% for the effluents. Since no colour reduction was measured in the control sample, the results confirm that colour reduction was due to ozone reactions.

The increase in BOD_5 was 5 to 6% for an ozone dose of 4 mg/L; but with further increase in ozone dose the BOD values decreased. This reduction was about 40 mg/L which corresponds to 20% for an ozone dose of 48 mg/L. The reduction in BOD_5 can be expressed as:

$$\ln (BOD_5 \text{ removed}) = 0.86 \ln (\text{ozone applied}) + 0.28 \quad (3)$$

It was extrapolated that application of 150 to 175 mg O_3/L would remove 90% colour and about 61 to 66% of BOD_5 from the effluent. The initial increase in BOD5 at lower ozone doses was believed to be due to degradation of larger molecules to biodegradable compounds. Along with the reduction in BOD5 and colour some reduction in TOC was also noticed. The average reduction in TOC was 0.25 to 0.3 mg per mg of ozone. The control experiment with pure oxygen showed no changes in BOD5, TOC and colour. The results also indicated that there was no sequential attack by ozone on various effluent parameters. However, colour was removed most readily; the degree of removal per unit ozone decreased logarithemically with increasing ozone dose. BOD was not as readily removed and TOC was slightly affected. The toxicity removal was attributed to foam separation which occurred for all the experiments and ozone had no apparent effect.

Nebel et al. (1974) studied the ozone treatment for the removal of colour for secondary effluents from four different sources. In addition to colour reduction the added advantages of ozonation were disinfection, reduction in COD and turbidity removal. The BOD was studied for the samples from the kraft process mill. Initially BOD contents decreased rapidly up to an ozone level of 40 mg/L. However, it increased at higher ozone doses and finally reduced again at further ozone doses of about 150 mg/L. It was interpreted that the initial BOD reduction was caused by the ozone oxidizing the readily biodegradable

compounds occurring in the effluent. Thereafter, the ozone attacked refractory compounds, principally degrading lignins, making them biodegradable. It was believed that ozone attacking the molecules introduces functional groups onto the refractory compounds. These new oxygen-containing groups offer bacteria a sight where metabolism could start, hence increasing BOD. Further application of ozone oxidized the degraded materials and resulted in a decrease of BOD.

Colour was the most dominant parameter affected with ozonation. The mechanism of colour reduction was believed to be either breaking down and / or altering the colour causing compounds in such a way that the degraded molecules absorb no light or less light in the visible range. They also underlined that ozonation process for colour removal did not produce sludge as opposed to the coagulation or lime treatment.

The economic analyses indicated that the ozone treatment might be cost effective for the pulp and paper mills. The major cost factor in the ozone generation is the cost of power. For the pulp and paper mills with large power requirements, the cost might be in the range of $0.08 to $0.09 /Kwh (based on 1974). Ozone generators have a 40% leading power factor whereas a pulp mill has a large lagging power factor. The combination of leading and lagging power factor would produce a power factor close to unity. This essentially means that the plant would utilize more of the power it had purchased and return less to the power plant. It was expected that the plant efficiency to utilize the power would improve.

Furgason et al.(1974) studied colour and odour reduction for four streams of effluents from a kraft process pulp mill. The experiments were conducted both on batch and pilot scale units. The batch experiments were run in a 2-L glass diffusion column. The colour reduction for an ozone dose of 550 mg/L to secondary effluent was 2820 APHA units which corresponds to 76% reduction.

The pilot run results indicated complete odour and 75 to 80% colour removal for an ozone dose of 200 mg/L and a residence time of 10 minutes in a pilot scale unit. The reduction in COD was 15%. The reduction in colour was rapid at residence time less than 10 minutes, and then decreased slowly thereafter.

The economic analyses for colour removal estimated the cost of treatment about $0.40 /1000 gal., are substantially lower than the $1.17 / 1000 gal. reported for reverse osmosis system, but substantially higher than the costs of lime treatment. The total cost of massive lime treatment at the Riceboro, Georgia, plant was reported to be $3.00 / ton of pulp. These costs would be equal to about $0.15 /1000 gal. if 20,000 gal./ton pulp were consumed. The $.40 / 1000 gal. treatment costs were based on 60% utilization of ozone charged into the system, and it was expected that they would be reduced by $0.09 / 1000 gal. if the ozone utilization could be improved by another 25%. The simplicity of the ozone system makes it possible to use it with selected highly coloured and odorous streams. For such a situation the economics might appear better.

Smith and Furgason (1976) studied the effect of ozonation on oxygen utilization rate of total plant effluent from a kraft mill. Since the lignin derivatives in the effluent consist of phenolic-type materials with chlorinated and sulfonated side chains, it was expected that ozone would alter the basic structure of these compounds and significantly change the biodegrability of the wastewater. The oxygen uptake rate was studied in a 1600 mL system using undiluted ozonated and unozonated samples to see the combined effects of ozonation and toxicity on biological treatment. Another set of oxygen uptake rate studies were conducted in 300 mL bottles using diluted effluent. These runs were used to examine the biodegradability eliminating toxicity effects.

A mathematical model was formulated to describe the oxygen uptake by microorganisms. The total oxygen uptake rate may be given by:

$$dO / dt = k_1 S + k_e X_a \qquad (4)$$

where:

O = dissolved oxygen concentration, (mg/L);

S = substrate's concentration, (mg/L);

X_a = active mass concentration, (mg/L);

K_1 = synthesis energy rate constant, (1/d);

k_e = endogenous rate constant, (1/d); and

t = time, (d).

Assuming both S and X_a follow first order removal functions:

$$S = S_o \exp(-k_r t) \quad (5)$$

and

$$X_a = X_{ao} \exp(k_{er} t) \quad (6)$$

where:

S_o = initial substrate's concentration, (mg/L);

X_{ao} = initial active mass concentration, (mg/L);

k_r = substrate's removal rate constant, (1/d); and

k_{er} = endogenous removal rate constant, (1/d).

When expressing the substrate's concentration S, and the active cell mass Xa in terms of oxygen concentration units, $k_1 = k_r$ and $k_r = k_{er}$, the oxygen uptake rate equation becomes:

$$dO / dt = k_r S_o \exp(-k_r t) + k_{er} X_{ao} \exp(-k_{er} t) \quad (7)$$

The magnitude of k_r, substrate's rate constant indicates the biodegradability of the material. The values of k_r were obtained by plotting dO / dt vs time. Since it was not possible to generate the same active mass X_a during each experiment , the biodegradability was judged by comparing the substrate's rate constant per unit of active mass k_r / X_a.

The results of oxygen uptake rate in 1600 mL system indicated a steady increase in the substrate's removal rate constants up to about 500 mg /L ozone dose, then after that it became scattered. However, in all the ozonated samples the rate of substrate's utilization was higher than

unozonated samples indicating a significant improvement in the ability of microorganism to utilize the material.

Ozonated and unozonated samples were run in 300 mL bottles for oxygen uptake rate studies to examine whether the improvement shown in 1600 mL system was due to breaking of larger molecules or due to toxicity removal. In the 300 mL bottles the oxygen uptake rate showed little difference for unozonated and ozonated samples. This behaviour was explained as follows; the ozonation process reduced the toxicity of the mill effluent but did not substantially change the basic biodegradability of the material. It was concluded that ozonated samples were more readily consumed by the microorganisms, colour reduction was 70 to 80% for an ozone dose of 200 mg / L and noxious odour was completely removed after ozonation. Ozonation process might not be economical for the total effluent, but could be an alternative to lime treatment for selected wastewater streams.

Melnyk and Netzer (1975) conducted a kinetic study of the reaction between ozone and lignin compounds which produce intense colour in bleach pulp mill effluent.

The objective of the study was to develop the kinetic model such that the ozone requirements could be optimised for the treatment process. It was noted that amount of ozone required was the controlling factor to make the ozonation process more attractive.

Experiments were conducted in a batch reactor and while the kinetic model was developed for the colour removal with the following assumptions:

1. colour was contributed by two species having different reactivities with ozone;
2. the total colour concentration was the sum of individual concentrations;

$$C_T = C_A + C_B \quad (8)$$

3. each species reacts with ozone as first order reaction;

$$dC_A / dt = K_A C_A \quad (9)$$

$$dC_B / dt = K_B C_B \quad (10)$$

after time 't'

$$C_A = C_{Ao} \exp(-K_A t) \quad (11)$$

$$C_B = C_{Bo} \exp(-K_B t) \quad (12)$$

f_o = total colour in the effluent

$$\text{Initial colour concentration } C_{Ao} = f_o * C_{To} \quad (13)$$

$$\text{Initial colour concentration } C_{Bo} = (1-f_o) * C_{To} \quad (14)$$

$$C_T = f_o C_{To} \exp(-k_A t) + (1-f_o) C_{To} \exp(-k_B t) \quad (15)$$

where C_T is the total colour remaining in the effluent after time 't'.

With another assumption that the rate of colour removal for both the species A and B was linearly dependent upon the soluble ozone concentration. The kinetic model was modified by substituting:

$$K_A = K'_A C_{O_3} \quad (16)$$

$$K_B = K'_B C_{O_3} \quad (17)$$

where:

C_{O_3} = Ozone concentration, (mg/L)

Assuming that the concentration of ozone remained constant during each experimental run the final form of the model was presented as:

$$C_T = f_o C_{To} \exp(-K'_A C_{O3} t) + (1-f_o) C_{To} \exp(-K'_B C_{O3} t) \quad (10)$$

The results based on the model suggested that there are at least two unidentified chromogenic species responsible for the colour in the kraft mill effluent. The more reactive species was responsible for 65 to 87% of the total colour.

Oxygen uptake rate which was monitored in a continuous respirometer indicated that ozone increased the total quantity of biodegradable material, but the new material degraded at a slower rate. It was also noted that increasing the period of ozonation decreased the total quantity of biodegradable material, because of the total oxidation of some of the material by ozone.

There was correspondingly smaller decrease in COD with ozonation compare to colour removal. COD decreased rapidly in the beginning and then decreased slowly. It was interpreted that ozone removed colour by altering the structure of the molecules rather than oxidizing them completely.

Buley (1973) looked into the application of ozone in the pulp industry. Colour and COD reduction was studied in a batch reactor for bleach stream, spillway and oxidation pond stream at pH between 3 and

5.5. Ozone was applied at 1.8% wt / wt concentration for 10 minutes. For the applied doses of 70 mg /L for oxidation pond effluent, 125 mg/L for spillway stream and 110 mg /L for bleach effluent, 98% reduction in colour was achieved. The corresponding decrease in COD was 38 mg/L, 81 mg/L and 141 mg/L, respectively. To minimize the ozone consumption for colour removal, it was suggested that ozone should be applied to the effluent after it had undergone all the treatment processes.

Dorica and Wong (1979) found ozonation a promising treatment for detoxification of linerboard effluent at relatively low chemical cost. The studies were aimed to investigate the toxicity and colour removal of the effluent after giving the following treatments:

1. precipitation with lime;
2. coagulation with alum;
3. combination treatment with powdered activated carbon (PAC) and lime;
4. combination treatment with PAC and alum; and
5. ozonation.

Preliminary results indicated that aeration in the presence of 200 mg/L PAC followed by 70 mg/L alum, aeration in the presence of 200 mg/L PAC followed by 1000 mg/L lime or 78 mg/L ozone on filtered effluent at pH 7.0 was adequate to detoxify the effluent. An 80 to 90% colour removal and 20 to 25% reduction in COD and BOD could also be achieved during the first three treatment processes. Ozonation resulted in 20 to 25% reduction in BOD and reduction in suspended

contents was also noted. Effluent treatment with lime or alum by itself did not remove the toxicity significantly. Lime treated effluent was rather, more toxic than untreated effluent, and showed colour reversal in the stabilization pond. Ozone was more effective to detoxify the filtered sample than unfiltered effluent. Preliminary cost of ozonation to detoxify the linerboard effluent with an ozone dose of 10 mg/L was estimated at about $.65 / adt (air dry tonne) pulp. The cost included equipment, power and liquid oxygen for ozone generation.

Prat et al.(1989) examined the ozonation of a bleach stream from a kraft mill for colour removal. The samples used were from alkaline extract of chlorine bleaching with 3288 colour units and 1721 mg/L COD. The experiments were carried out in a bubble reactor with a cocurrent circulation of gas and liquid and exterior refrigeration.

The results indicated that there were at least three classes of compounds with different reactivity towards ozone. The first group of compounds were decolourized quickly with ozone and constitute about 90% of the total colour. The second group of compounds which were about 10%, decolourized very slowly. It was observed that after total decolourization there was still an ozone demand. This uncoloured compounds were classified into third group. It was estimated that the rate constant for first group of colour causing compounds was 26 times higher than the second group of compounds, therefore it would only be economical to decolourize the effluent for the removal of first group of compounds unless it was possible to achieve some other benefits with prolonged ozonation.

Sozanska and Sozanski (1989) conducted a comparative study of 1) ozonation, 2) ozonation with alum or lime coagulation as prior step and 3) ozonation with chlorination as a prior step for pulp mill secondary effluent. Ozonation was carried out in a column reactor with countercurrent flow of ozone and the effluent. During the experimentation the sample BOD_5 varied between 7 mg/L and 180 mg/L. The variation in COD and colour was between 164 to 367 mg/L and 250 to 700 colour units, respectively.

Ozonation alone required higher ozone doses for colour reduction. Colour removal was satisfactory when the ozone dose exceeded 50 mg/L. The reduction in COD was very small compared to colour reduction. For an initial value of less than 23 mg/L, the BOD_5 increased with ozonation, but for high initial values, BOD_5 decreased with ozonation. Ozonation process also removed the specific odour from the secondary effluent.

Treatment with 150 to 350 mg/L alum prior to ozonation improved the efficiency significantly. Alum coagulation yielded better COD and BOD_5 removal, whereas ozonation accounted for higher colour removal. After alum coagulation small amounts of ozone was sufficient to deodorize the effluent completely. Lime treatment prior to ozonation also produced good results, but the required lime dose was in the range of 400 to 650 mg/L to raise the pH to about 12 and achieve the desired effects. However, alum coagulation was more effective than lime treatment.

Chlorination as a prior step to ozonation yielded lower removal efficiencies. Addition of 100 mg chlorine/L to the effluent either decreased the colour slightly or, in some experimental runs increased the colour by about 20% as well as increased the BOD5. Chlorination removed the specific effluent odour, but a distinct timber odour was persistent. Chlorination produced trihalomethanes. Their concentration varied between 223 to 517 µg/L (chloroform accounted for 217 to 480 µg/L). Ozonation after chlorination reduced the colour, and increased BOD5. The concentration of trihalomethanes was reduced by 33 to 53%.

Ozonation alone yielded good removal efficiencies of colour, odour, lignins, tannins, humic acid, fulvic acid and anionic surface active substances, but the ozone dose required was about 80 mg/L. After the alum coagulation step, the ozonation process efficiency was significantly improved and ozone demand was reduced by about 30 mg/L. Alum coagulation and lime treatment improved the efficiency of ozonation process whereas, chlorination decreased the efficiency.

2.7.7 Effect of Ozone on Dioxins

Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans(PCDF) discharges in the kraft process pulp mill effluent have caused great public concern. Their concentrations are not very high compared to other sources of emissions such as municipal incinerators etc., but due to their inert nature, adsorption on suspended solids and bioaccumulation characteristics they cannot be ignored at any level of discharge. PCDD and PCDF are almost inert in the

presence of acids and alkali solutions and are, under certain conditions, chemically stable against oxidative and reductive reaction conditions, and are stable at high temperatures (several hundred °C) (Mark et al. 1987).

Waterborne 2378-TCDD (tetrachloro dibenzo-p-dioxin) and 2378-TCDF (tetrachloro dibenzofuran) are very toxic to fish; respectively 10,000 and 1,000 times more than the insecticides previously considered to be the most toxic chlorinated hydrocarbons (Bonsor et al. 1988). Typical fish in mill effluent streams showed adverse effects to concentrations between 10 and 60 ppt, while studies indicated a concentration of 930 ppt is required to affect growth (Bonsor et al. 1988). However, 2378-TCDF is strongly bioaccumulative and bioaccumulation in predatory animals must be of concern.

The acceptable daily intake (ADI) of 2378-TCDD is estimated to be 0.7 ng/d for a 70 kg human (Bonsor et al. 1988). In a worst case scenario it is possible for a frequent fish eater, who is eating fish caught downstream of a mill, to receive more than the ADI. Dioxins and furans are proven to extremely toxic to mice, rats and other test animals, but lethal doses have varied by over three order of magnitudes between the species (Tschirley 1986). There have been hundreds of human exposures, but no consistent picture of effects such as cancer, heart disease, reproductive problems is available (Bonsor et al.1988); transient skin eruption known as chloracne are the most consistently documented health effect (Tschirley 1986).

Ozone as a very strong oxidant, can react with PCDDs and PCDFs. Mark et al. (1987) studied the degradation of dioxins with ozone in an aqueous medium and in a typical dump leachate at pH 5 and 10. At pH 5 no significant degradation of 2378 T4CDD was detected, but ozonation at pH 10 resulted in an obvious decrease in dioxins' concentration. In acidic conditions ozone molecule appear to attack mainly the double bonds, whereas OH radicals formed in the alkaline conditions attack unspecifically on the carbon skeleton or functional group in the dioxin molecule. The data also indicated temperature effects; 90% degradation was achieved after 60 minutes of reaction time at 20° C. At 50° C the degradation was considerably faster and required 30 minutes for about 90% degradation of 2378 T4CDD.

Another set of experiments conducted with dump leachate indicated that ozonation was equally effective for the removal of dioxins. At pH 10, 88% degradation of T4CDD was measured.

These results show the versatility of ozone for treating the pulp and paper mill effluent. It not only removes colour, odour, surface active compounds, toxicity; but improves BOD and effluent in many more ways which are still unknown.

2.7.8 Equipment

Ozone contacting devices or reactor is one of the most important parameters in the effectiveness of ozone application. Since ozone does not react with the compounds selectively, it is necessary to have an effective ozone transfer system such that the required parameter of the effluent is removed during the treatment process. An effective reactor

can give a better handle on the applied dosage and the results can be correlated with the amount of ozone applied. The efficiency and the amount of ozone required for a particular improvement is the major factor which governs the economics of the ozonation process.

Most of the reactors, used in the previous studies, have been semi-batch type i.e. taking the effluent in a reactor and allowing the ozone gas mixture through it for a set time period. Some of the studies were carried out in continuous flow reactors.

Bauman et al.(1974) conducted experiments in a continuous column type of reactors. The set up consisted of four contact towers 200 mm in diameter. Effluent could be regulated at 0 to 5 gal/min. Most of the studies were conducted at 4 gal / min flow rates which gave a retention time of 7 minutes in each tower. 40% ozone was applied in Tower 1, 30% in Tower 2 and 20% in Tower 3 and 10% in Tower 4. Gas flow rates were regulated so that ozone was not released from the tower. Each column was provided with sampling valves and foam overflows.

Ng et al.(1978) used a dynamic system which consisted of a contact tower type of reactor. The reactor consisted of a 3-m length and 150 mm diameter PVC column containing a concentrically mounted 100 mm diameter pipe sealed to the 150 mm pipe at the lower end. The inside pipe provided a good contact between ozone and the effluent and reduced channeling. The effluent was recirculated through the contact column. The residence time in the contact column was 2 minutes and each passage introduced 8.8 mg/L of ozone. Thus by

repeating the passage through contact column, the ozone dose was regulated.

The studies were also conducted in a batch reactor consisting of a 40-L container fitted with a fine pore-size (fritted glass) dispersion tube. Ozone was dispersed into the effluent and mixed with a magnetic stirrer. Residual ozone in the exit gases was absorbed by potassium iodide solution and estimated.

Nebel et al.(1974) used a column reactor provided with a porous diffuser for ozone distribution in the system. The outgoing gases were trapped in potassium iodide solution and measured for residual ozone.

The experimental set-up used by Furgason et al. (1974) consisted of a rotameter for measuring liquid flow rate, a reaction vessel, a recycle pump for the effluent, and a venturi gas-liquid contactor for ozone application. Two reaction vessels having volumes 14 L and 57 L were available for the reaction. A wide range of residence times were obtained by changing the reaction vessel, adjusting flow rates and liquid levels in the reaction vessel. The ozone dose to the effluent was controlled by adjusting the recirculation rate, such that a higher recirculation rate would result in a higher ozone dose. Small amounts of silicone antifoaming agent was added for foam control.

Melnyk and Netzer (1975) applied the ozone dose to a batch reactor. The reactor consisted of a round bottom glass cylinder of 1-L capacity and a coarse sintered glass sparger. Ozone was applied through sparger and the exit gases were collected in potassium iodide solution traps to estimate residual ozone. The gas flow rates were maintained

with the help of a rotameter and needle valve between 0.5 to 2.0 L / min. At these flow rates, the applied ozone was being used up and no residual was detected.

Dorica and Wong (1979) used a continuous reactor for their ozonation studies. It was a glass column, 1200 mm in length and 76 mm in diameter. Ozone (2% O_3, 98%O_2) was sparged into the bottom of the column. The reaction time was controlled by adjusting the height of the liquid column. The exit gases were analysed using the potassium iodide method for residual ozone.

The reactor used for decolorization studies by Prat et al.(1989) was bubble type with cocurrent circulation of gas and liquid effluent. The reaction zone consisted of a cylindrical quartz tube, 1000 mm in length and 22 mm in diameter. This system provided perfect mixing conditions in the reactor due to high recirculation rate whereas, the gas phase was in a plug flow mode.

Soznaska and Sozanski (1989) conducted their experiments in a cylindrical reactor with an expanded top portion to facilitate liquid and gas separation. Ozone was applied through a sparger in the bottom of the reactor, while the effluent was countercurrently introduced to the top. Potassium iodide technique was used for ozone determination, and ozone flow rate was controlled by a rotameter.

In all the studies, the experiments were conducted in a semi-batch, or continuous reactor, applying ozone through sintered glass sparger continuously and measuring the dosage based on flow rate,

concentration and time. Most commonly, potassium iodide method was used for ozone estimation.

3.0 MILL OPERATIONS

For this study samples were collected from Weldwood Canada Ltd, Hinton, Alberta. The mill produces 500 tonne / day of bleached pulp using the Kraft process. The raw material consists of 50% lodgepole pine, 40% white and black spruce and 10% alpine fir.

3.1 Pulping Operation

Wood chips are cooked with 65% NaOH, 25% Na_2S and 10% Na_2CO_3 at 160° C and 1150 KPa for about 2 1/2 hrs for pulping purpose.

3.3 Bleaching Operation

The cooked pulp which is dark in colour is bleached to improve the brightness and remove remaining lignin. The six stage bleaching sequence employed at the plant consists of: chlorine, caustic extraction, hypochlorite, chlorine dioxide, caustic extraction, and chlorine dioxide. With the bleaching process, whiteness of the pulp is improved from 30 (brown) to 90+ (snow white) level. After each bleaching stage the pulp is thoroughly washed in a rotary vacuum washer to remove the residual chemicals. Since large quantities of water are used for washing purposes, and the concentrations of the chemicals are very low, the chemicals are not recovered. Essentially all the washing water goes either to alkali or acid sewers.

Chlorine and caustic are purchased, the other chemicals required for bleaching are manufactured at the plant. Sodium hypochlorite (NaOCl) is manufactured on a continuous basis by bubbling chlorine gas through a caustic solution, ClO_2 is manufactured by reacting

$NaClO_3$, H_2SO_4 and SO_2. SO_2 gas is manufactured continuously by burning elemental sulfur.

3.4 Chemicals Recovery

The cooking liquor is concentrated in the evaporators from 14% solids to 70% solids. The concentrated liquor is burnt in recovery boiler where the organics are removed and inorganics form Smelt, which is recycled into the process.

3.5 Wastewater Treatment Facilities

Plant effluent undergoes primary and secondary treatment for the removal of suspended solids, soluble BOD and render the effluent nontoxic (Figure 2).

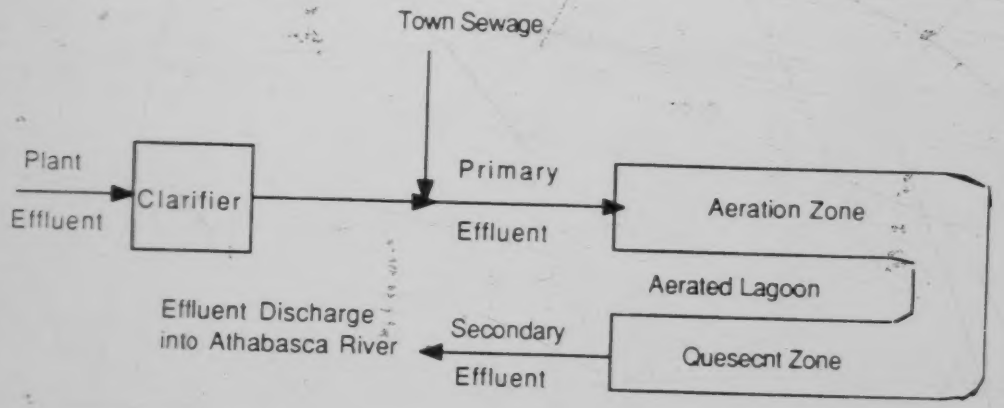

Figure 2. Wastewater Treatment Facilities at The Pulp Mill

All mill effluent except the bleach plant acid sewer passes through a circular primary clarifier of about 60 m in diameter. Some of the wastewater from the acid sewer is added to the mill effluent before

the clarifier to lower the pH to 8. The solids which settle out are removed as sludge, dewatered in the solids handling section and trucked to landfill. Further acid sewer wastewater is added to the clarifier overflow to bring the pH to 7.0 before entering the secondary treatment lagoon. Since the mill effluent is deficient in nitrogen and phosphorus, nitrogen is added in the form of urea in the clarifier. The phosphorus requirements are fullfilled when the mill effluent is combined with town sewage.

Secondary treatment consists of a U-shaped lagoon, having a 4.6 m to 6.0 m depth. The north arm of the lagoon contains 13 surface aerators with a total horse power of 1425, and the south arm serves as a quiescent zone after aeration. Theoretical detention time of the aerated lagoon is 5 days. The mill treatment facility also handles all the sewage from the town which is approximately 5000 m^3/d and accounts for between 5 and 6% of the plants' effluent. This waste is mixed with the clarifier effluent and flows into the aerated lagoon.

The treated effluent and remaining acid sewer wastewater from bleach plant are mixed and flow down a rocky slope to a foam trap at the river edge. Final effluent is discharged into the Athabasca River through a sparger pipe which runs across the width of the river and is discharged at a rate of 93000 m^3/d.

4.0 EXPERIMENTAL PROTOCOL

4.1 Wastewater Streams Characterization

Effluent streams were characterized for physical and chemical parameters before the ozonation studies. During the ozonation phase the ozonated and unozonated samples were evaluated for the effects of ozonation on the characteristics of primary, bleach and secondary effluents.

4.1.1 Sampling

The procedures for sample collection, handling, trannsportation, storage and preservation as outlined in Standard Methods 1985, and WPCF 1980, were used during the study.

Arrangements were made with the plant personals for collection and shipping of samples to Edmonton. A grab sample from bleach section was collected directly from the alkaline extraction unit. The plant has arrangement for collection of 24-h composite samples of primary and secondary effluents for licensing purposes. These samples are collected by a time based auto samplers and analyzed for regulatory and wastewater treatments' operational reasons. The 24-h composite samples at the plant were mixed, and the lines were flushed thoroughly before transfering into 1-L glass bottles, which had earlier been acid washed, rinsed thoroughly with distilled water and dried. For shipping purposes, the bottles were stacked in a cooler and stuffed with ice to reduce the biodegradation of the samples during transportation. As the samples arrived at Edmonton, they were

collected without delay and brought to the laboratory. In the laboratory, the samples were stored at 4° C overnight, and the experiments were conducted next morning. The samples evaluated during the course of study are given in table 2.

Table 2. Samples Evaluated During the Ozonation Study

Sample	Effluent	Nautre of Sample	Temperature (° C)	pH
1	Bleach	Grab	52	11.3
	Acid Sewer	Grab	45	5.9
	Primary	24-h Composite	39	7.2
	Secondary	24-h Composite	33	7.2
2	Bleach	Grab	44	10.8
	Primary	24-h Composite	35	6.8
	Secondary	24-h Composite	32	7.1
3	Bleach	Grab	38	10.2
4	Primary	24-h Composite	33	6.3
5	Secondary	24-h Composite	20	7.1
6	Secondary	24-h Composite	10	7
7	Secondary	24-h Composite	27	7.2

4.1.2 Analytical Procedures

Table 3 summerizes the parameters and the analytical methods used to characterize the wastewater streams.

Table 3. Water Quality Parameters to Characterize wastewater Streams from a Kraft Process Pulp Mill

Parameter	Method	Reference
Temperature	212	Standard Methods, APHA,AWWA, WPCF, 1985
pH	423	Op. cit
Total Coliform	909A	Op. cit.
TSS	209 C	Op. cit
VSS	209 D	Op. cit
BOD-Bottle	507	Op. cit
Respirometer		Operational Manual for Gilson Respirometer
COD	508A	Standard Methods, APHA, AWWA, WPCF, 1985
TOC	505B	Op. cit
TOX	506	Op. cit
Kjeldahl Nitrogen	420A	Op. cit
Phosphorus	424F	Op. cit
Ozone Residual	422	Op. cit
Colour		NCASI, 1971

TSS = Total Suspended Solids
VSS = Volatile Suspended Solids
BOD = Biochemical Oxygen Demand
COD = Chemical Oxygen Demand
TOX = Total Organic Halides
TOC = Total Organic Carbon

4.1.2.1 pH

The pH of the samples was measured at the plant laboratory using pH meter before shipping the samples to Edmonton. The meter was calibrated using pH 7 and 10 standards.

4.1.2.2 Temperature

Similarly, the temperature of the samples was recorded at the mill and the data sent to Edmonton along with the samples.

4.1.2.3 Colour

Precautions taken to allow the reproducible results were:

1. Same spectrophotometer was used through the studies.
2. To achieve the stability of the instrument, the spectrophotometer was run an hour before measuring the absorbance.
3. The cuvets used for measuring absorbance were washed with chromic acid, rinsed thoroughly with distilled water, and dried for each set of experimentation.
4. For preparing colour standard graphs, standard colour solution having 500 colour units, supplied by Fishers Chemicals, was diluted to required colour levels.
5. Colour standards were carefully preserved to prevent any loses due to evaporation.
6. For each set of experiments, colour standards were run and plotted, the same colour standard graph was used for the colour measurements of that particular set of samples.

7 Milli-Q water was used for the blank.

4.1.2.4 Suspended Solids

Prior to ozonation experiments, the filter papers were washed, dried weighed and preserved in a desicator. These preweighed filter papers were used for suspended solids analysis.

4.1.2.5 Biochemical Oxygen Demand (BOD)

4.1.2.5.1 Preparation of Dilution Water

60-L of Milli-Q water was taken in two carboys which had earlier been washed with deionized water and rinsed three times with Milli-Q water. The dilution water was aerated for about 12-hr to reach saturation with oxygen, and left for about 4 to 6 hours to make sure that all the excess dissolved oxygen was released. Before starting the BOD analysis 1 mL each of phosphate buffer, magnesium sulfate, calcium chloride and ferric chloride solutions were added per litre of the dilution water. 1 mL laboratory acclimatized seed and 10 mg allyl-thio-urea as a nitrogen inhibitor were also added per litre of the dilution water and the contents were aerated for a few minutes to disperse the nutrients, nitrogen inhibitor and the seeds homogeneously.

4.1.2.5.2 Acclimation of Seed

Laboratory acclimatized seed were used for BOD test. Seed were acclimatized for primary, bleach and secondary effluent in seperate units.

4.1.2.5.3 Toxicity and Inhibitory Effects

BOD tests were conducted to find the appropriate dilution, to eliminate the effects of toxicity.

4.1.2.5.4 Nitrification Inhibition

10 mg / L Allylthiourea (ATU) was added to dilution water for nitrogen inhibition. The degradation of allythiourea is slow and no significant error should occur in the BOD determination (Young 1973). Further the problem of degradation of ATU is controlled by titrating the BOD bottles immediately after adding the sulfuric acid to liberate iodine (Young 1973).

During the present investigations all the BOD test were conducted in a way that sulfuric acid was added to one bottle at a time, and the liberated iodine was titrated immediately.

4.1.2.5.5 Dilution Technique

To achieve a uniformity in the dilution, and reduce the error in the preparation of individual bottles, a graduated cylinder was used for preparing the dilutions for BOD tests.

For setting up the BOD bottles, a 2-L graduated cylinder was half filled with dilution water and the required amount of sample, say 40-mL of bleach effluent was added with a wide-tip volumetric pipette to the cylinder. The graduated cylinder was then filled to the mark. Mixing the contents thoroughly with a three-blades PVC coated plunger type of stirrer, the solution was transferred into a 4-L beaker. Two more litres of dilution water as required, were added to the beaker and the contents were thoroughly mixed with the stirrer. For

preparing BOD bottles for incubation, the diluted sample was carefully siphoned out of the beaker into the bottles, while stirring the contents slowly, such that a homogeneous solution could be added to each bottle. For initial oxygen demand determinations, three bottles were selected randomly and titrated after a lapse of 15 minutes. The same dilutions were prepared for seed to subtract the oxygen demand from the samples' BOD.

For bleach and primary effluent, lower dilutions were used for 20-day BOD test to avoid total depletion of oxygen.

Three bottles each were titrated for initial DO, 5, 7, 10 and 20-day BOD and one bottle each was titrated for 2,3,4 and 6-day BOD determinations.

4.1.2.6 Chemical Oxygen Demand (COD)

The COD tests were conducted as follows:

1. $HgSO_4$ 0.4 to 0.5 g.
2. Sample volumes: 10 mL each of bleach or primary or secondary effluents.
3. Dichromate solution: 25 mL for bleach sample, and 10 ml each for primary and secondary effluents.
4. $AgSO_4$ / H_2SO_4 reagent: 30 mL.
5. Few glass beads.
6. Reflux time: 2 hours.

4.1.2.7 Total Organic Carbon (TOC)

Mercuric salts (chloride and nitrate) were added to a 2% potassium persulfate solution for reducing the interference of chloride.

Inorganic carbon was also determined, and the value was deducted for obtaining TOC and DOC.

4.2 Experimental Program

To identify the relative suitability of ozone application location three major effluent streams from the mill were selected. The effluents were;

1. alkaline extract of bleach stream, responsible for 75% of the total colour and almost all the organochlorines;
2. primary effluent, combined with town sewage and before entering the treatment lagoon;
3. secondary effluent, before the outfall.

As mentioned, objectives of the present study were to look into the improvement in the biotreatability and BOD of the mill effluents, and identify the effluent with which ozone application would produce the most significant improvements in the overall treatability. The biotreatability studies were conducted by setting up the BOD test for ozonated and unozonated samples. A control experiment was conducted by applying pure oxygen in place of ozone to check, if oxygen by itself had any effect on the parameters of interest.

BOD test is a very specific test, and is supposed to be conducted with a population of well acclimatized microorganisms. In general large discrepancy and low reported BOD values for industrial wastewater is mainly due to the use of non-acclimated biological seed in the BOD test (Eckenfelder, 1966). The other factors which influence the BOD test are; presence of toxicity and inhibitory effects. Therefore

it is essential to remove these effects by using well acclimated microorganisms as well as finding the proper dilutions at which the toxic and inhibitory effects are minimized.

The ozonation studies were divided in four stages:

1. seed acclimation;
2. optimization of dilution for BOD test;
3. characterization of the effluents; and
4. ozone application.

For acclimatizing purpose, initial seed was obtained from the pulp mill laboratory and fed with bleach, primary and secondary effluents in separate acclimatization units. Thus the microorganisms were acclimatized for the particular effluent and used during the ozonation study for BOD estimations.

BOD test for all the samples were run at various dilutions and a suitable dilution was selected based on the test results. The same dilutions were used throughout the study for both ozonated and unozonated samples to have a common basis for comparison of results.

Bleach and primary effluents were treated with 50 and 100 mg/L ozone doses, whereas, secondary effluent was applied between 50, 100, 150 and 200 mg/L of ozone.

4.2.1 Objectives

As a strong oxidant, ozone is expected to react effectively with compounds in pulp mill effluent and improve the overall treatability.

Present studies were planned to see the effect of ozonation on kraft process pulp mill effluent with the following objectives:

1. improvement in biotreatability and effect on BOD, collecting data such that a good estimate of 'K', the BOD rate constant, and ultimate BOD could be obtained;
2. evaluate the effectiveness of ozone for colour removal for different wastewater streams; and
3. identify relative suitability of ozone application locations in the treatment process.

It was also intended to see the effects of ozone on chemical oxygen demand, total organic carbon and suspended solids of the mill effluents.

4.2.2 Experimental Design and Analysis

For ozonation study the experiments were designed and carried out on paired basis, which means setting up the ozonated and unozonated samples for parameter determinations under the same condition and then comparing the results. This method has the advantage of eliminating unwanted sources of variability (Box et al. 1978).

For ozonation studies, attempts were made to eliminate or reduce the errors during the experiments. Before starting the experiments, the sample which was shipped in 1-L bottles from the plant was mixed together in a large glass container and stirred thoroughly till homogenized. This was practiced for all the samples such that any possible variations in the composition of sample from

bottle to bottle were eliminated. All the experiments were run as genuine replicates. Duplicate experiments were conducted for bleach and primary effluent which did not show much improvement in biotreatability. Whereas for secondary effluent six experiments were conducted for 50 and 100 mg O_3/L doses to have enough data for calculating the standard error, and conducting 't' test. For each set of experiments an additional experiment was conducted with pure oxygen (instead of ozone) to verify the hypothesis that the changes observed in the ozonated samples were due to ozone alone, and the oxygen which was present with ozone was not responsible for them. The 't' test was used to check the statistical significance of improvements between different samples.

Before pooling the results for paired comparison the variance of individual samples was tested. Individual variance of the sets of data was calculated establishing the Null Hypothesis as:

$$Ho: \sigma_1^2 = \sigma_1^2$$

The data was also tested using ANOVA table for checking the significance of changes in the parameters with ozonation. Residuals were plotted to verify constant variance and normality assumptions.

The method of Non-linear Least Square was used for calculating K_e and L_o for the BOD model. The precision of the parameter estimate was evaluated by plotting the Joint Confidence Region (JCR).

The interpretation of the JCR is, smaller the joint confidence region better the estimates of K and L_o (Berthouex et al., 1971). To get a better estimate of parameters it is desirable to design the experiment

(Berthouex and Hunter, 1971). However, for first order reaction, the best estimates of parameters are obtained by the data at 1 / k and ∞ time.

The initial guess for K_e and L_o is important for their estimation, those values were calculated using Thomas graphical method (Metcalf and Eddy 1979) based on the function:

$$(t / y)^{1/3} = (2.3\ K\ L)^{-1/3} + K^{2/3} / 3.43\ L^{1/3}\ t \qquad (19)$$

4.3 Ozone Apparatus and Analytical Methods

4.3.1 Ozone Generator

Extra dry oxygen was used for producing ozone using Model C2P-9C-4 generator supplied by PCI Ozone Corp. The system was operated in accordance with the manufacturer instructions.

4.3.2 Ozone Concentration Measurement

Ozone concentration was measured at ambient temperature and pressure by means of a continuous monitor which operated on the UV absorption method (Model HC12; PCI Ozone Corp., N.J.). The concentration of the ozone in the gas stream is directly given in % wt / wt which could be converted to concentration units.

Ozone was also quantified using potassium iodide method as given in the Standard Method (APHA, AWWA, WPCF, 1985). However, a fritted glass diffuser was substituted for the V dimension tube specified.

4.3.3 Ozone Reactor

Previous studies on ozonation of pulp and paper mill effluent were conducted in a semi-batch or continuous reactor, applying ozone

through sintered glass sparger continuously and measuring the dosage of ozone based on gas flow rate, concentration and time. Most commonly, potassium iodide method was used for ozone estimation.

Continuous or semi-continuous flow reactors are good for pilot scale investigation when the actual designed parameters have to be determined. However, for getting the basic understanding of the ozonation process, more strict control on the process variables is essential. The short comings for continuous reactors are:

1. foam separation during ozonation, as reported in one of the studies, may introduce error in BOD determination, since the unozonated samples contain the foam fraction which was toxic in nature, whereas some of the toxicity was removed during ozonation;
2. ozone dose was measured using variables, such as gas flow rate, concentration and time; and
3. sintered glass spargers used for ozone diffusion have been reported to be responsible for some ozone decomposition (IOA 1987).

To overcome the above problems, a two phase reactor was designed to carry out the experiments. The reactor consisted of two distinct parts; the upper part of the reactor was a round bottom flask, while the lower part was a graduated cylinder for holding the effluent (Figure 3). The cylindrical part had a capacity of 500 mL, and the volume of the spherical section was about 1100 mL. Both the parts were joined together with a 6 mm thick walled T-joint. Opposite ends

of the T-joint were connected to the top and bottom parts of the reactor, while the third end of the T-joint was provided with a teflon stopper, to be used as the gas inlet to the reactor.

The neck part of the round bottom flask was a ground glass standard 24/40 tapered joint. The male end of the connector was also provided with a teflon sleeve to prevent any gas leakage. The other end of the joint was extended and tapered to 6 mm, where the teflon stopper provided was used as gas outlet for the reactor.

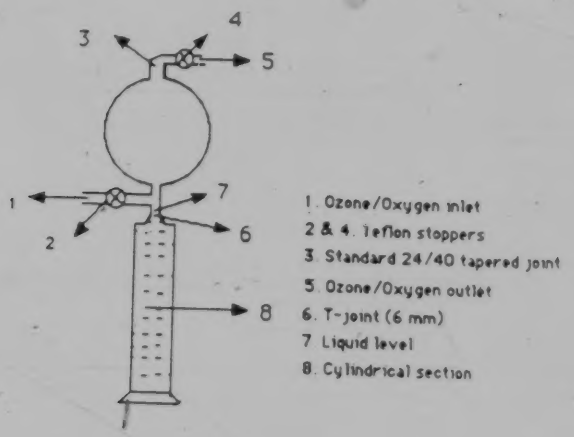

Figure 3. Reactor for Ozonation

4.4 Experimental Procedure

For the ozonation study, one sample at a time (bleach, primary or secondary effluent) was collected at the pulp mill and sent to Edmonton. Along with the sample for ozone study, 1-L of the other effluent streams were also collected and were used in the acclimatizing units. The sample, stored at 4° C, was allowed to reach room

temperature by letting it stand for a period of time before starting the experiment. The sample from the 1.0 L bottles was then mixed in a large glass container to achieve a uniform and consistent quality. This procedure was adopted to eliminate the quality variations from bottle to bottle and provide a uniform basis of comparison for ozonated and unozonated sample parameters.

4.4.1 Seed Acclimation

For present investigation initial seeds were obtained from the batch acclimation unit set up in the plant laboratory for the purpose of BOD determination. The acclimation units set up for ozonation studies consisted of three 1-L erlanmayer flasks, one each for bleach, primary and secondary effluent, connected parallel with a single air supply. The unit consisted of a 1-L erlenmayer flask with a two hole stopper. Through one hole a small glass tube was inserted such that the system was open to atmosphere. A longer glass tube was passed through the other hole. One end of the glass tube was connected to the air supply line and the other end had a diffuser stone for distributing the air in the form of fine bubbles through the acclimating seed and also provided uniform mixing. Air was supplied through a glass wool filter to arrest the particulates. The total air flow rate to the acclimation unit was about 120 mL/min. The levels of the effluent in each of the flask was maintained same such that the air supplied could be equally distributed in all three units. A small quantity of air was supplied to arrest the rapid growth of microorganisms, and maintain biological activity such that the oxidation of organic matter was slow and large

amounts of effluent would not be required to feed a larger population of microorganisms.

Initially 500 mL of seeds were added to each acclimatization unit, after every fourth day 100 mL effluent was added to each unit. When the total contents of the flasks reached between 800 and 900 mL, 100 mL of seed were wasted before adding 100 mL of the effluent to each unit. No pH adjustment was required for primary and secondary effluent, because the pH was already in the range of 6.8 to 7.2. However, the pH of bleach effluent was in the range of 10.5 to 11.5 therefore it was adjusted to about 7 before adding it to the acclimation unit.

Since the initial seed for acclimation unit had already been acclimatize to the waste, full strength primary and secondary effluents were added to the seed in the laboratory. The bleach effluent which was expected to be toxic to the seed, was added at a 25% dilution in the beginning which was slowly increased until it was full strength in three weeks. These acclimated seed were used for BOD test through out the studies.

When the seed had to be used for BOD tests, the air supply to that particular flask was cut off and the suspension was allowed to settle down for about 15 minutes. The supernatent liquid from the flask was drawn and used for the BOD test.

4.4.2 Optimization of Dilution

One of the reasons for erratic BOD tests results is the presence of toxic or inhibitory effects during the test. For comparing the BOD values before and after the ozonation, the BOD tests were conducted

such that it is not effected by toxic or inhibitory effects, and would be representative for the actual changes occurring in the BOD values due to ozonation. For this purpose BOD tests were conducted at various dilutions for each effluent, and a particular dilution was selected at which the toxic and inhibitory effects were at a minimum (Appendix I).

4.4.3 Characterization

During the acclimation period and optimization of the dilution stage, the effluents were evaluated for physical and chemical parameters, such as pH, temperature, colour, suspended solids, BOD(bottle method and respirometric), COD (filtered and and unfiltered), TOC (filtered and unfiltered), TOX, Total phosphates and kjeldahl nitrogen were determined in the beginning to have an idea about the concentrations levels of these elements present in the effluents. During ozonation studies the chemical and physical parameters were analysed for ozonated and unozonated samples.

4.4.4 Ozonation

During the first phase of the study, ozone was applied at a rate of 50 and 100 mg/L to bleach, primary and secondary effluents. The first set of experiments were conducted with bleach effluent, and the effects of ozonation on the effluent was studied. The second and third set of experiments were conducted for primary and secondary effluents, respectively.

Two genuine replicate experiments were performed for 50 mg/L and 100 mg/L ozone doses for bleach and primary effluents the

parameters were evaluated for ozonated, unozonated and oxygenated samples.

Secondary effluent, which showed significant improvements after ozonation, a total of six experiments were conducted to evaluate the results on statistical basis. Two additional doses of 150 and 200 mg O_3/L were applied to secondary effluent to further strengthen the results, and study the effects of higher ozone doses on the effluent parameters.

A control experiment was conducted by adding pure oxygen to the effluent sample. This experiment was conducted and set up in an identical way. Before the control experiment the ozone generator lines were thoroughly flushed for ozone traces.

4.4.5 Verification of Ozone Dose

For the required ozone dose of between 50 to 200 mg/L, the voltage, pressure and oxygen flow rate was adjusted to pre-determined values and the generator was allowed to run for stabilization. Once the ozone output had stabilized, 2% KI solution was placed directly in the cylindrical section of the reactor using a long stem funnel. The KI solution was filled in the T-joint up to the gas-inlet to reduce the ozone diffusion into the solution (Figure 3).

After passing the ozone/oxygen mixture for 5 minutes at a flow rate of 2 L/min both the stoppers were closed simultaneously entrapping the ozone gas in the spherical section of the reactor. The reactor was then disconnected from the generator and the KI solution was slowly transfered into the spherical section by tilting the reactor.

The reactor contents were mixed to achieve contact between the KI solution and the ozone gas. The mixing continued for 10 minutes to ensure complete reaction.

The ozone residual in the spherical section of the rector was tested by connecting the inlet of the reactor to a nitrogen purge set up. The outlet of the reactor was connected to a series of KI traps to arrest the residual ozone. After making the connections, the stoppers were opened and nitrogen gas was introduced into the reactor at a flow rate of 2 L/min, driving off the residual ozone in the reactor which eventually reacted with the KI solution in the traps (Figure 4). The KI solution was titrated with 0.005 M sodium thiosulfate solution to determine the ozone residual. It was found that 10 minutes of mixing time was enough for the ozone present in the reactor to react with the KI solution.

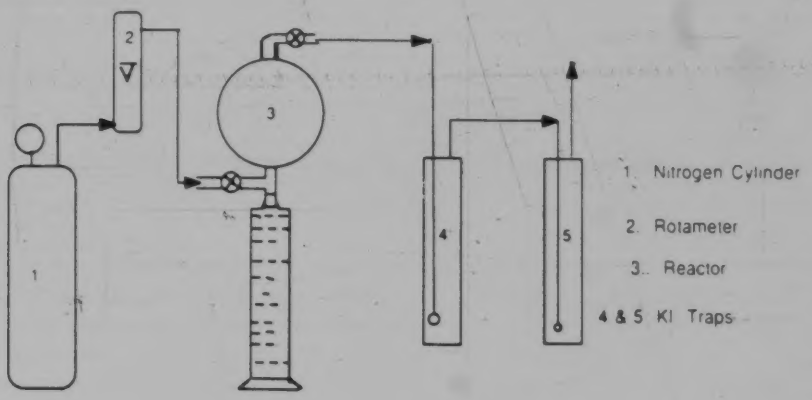

Figure 4. Nitrogen Purge Set-Up

The reactor was then disconnected from the nitrogen-purge set up and the KI solution was transferred into a conical flask. The KI solution was titrated with sodium thiosulfate to determine the total quantity of KI reacting compounds (mostly ozone) present in the reactor at the set voltage, pressure and oxygen flow rate. Since the required setting of the generator parameters had already been established by the UV monitor, two additional titrations were adequate to ensure correct ozone dose. The above procedure was repeated for all the ozone doses

4.4.6 Measurement of Amount of Ozone Diffused into Cylindrical Part of the Reactor

For measuring the amount of ozone diffused into the cylindrical section of the reactor while passing the ozone / oxygen mixture to repleace the air from the spherical section, KI solution was taken into the cylindrical section. Ozone / oxygen mixture was passed through the spherical section by connecting the inlet of the reactor to ozone generator. After 10 minutes, the reactor was disconnected from the generator and connected to nitrogen purge system (Figure 4). Nitrogen, at a flow rate of 3 L/min was passed through the reactor to drive off the ozone present in the spherical section of the reactor. The KI solution was then transfered into a volumetric flask and titrated with 0.005 M sodium thiosulfate solution to determine the amount of iodine liberated during the reaction with diffused ozone. The calculation are given in Appendix VIII.

4.4.7 Ozone System Calibration and Reactor Design

In the second phase of study different reactors were investigated. Eventually the batch reactor was developed for ozonation studies (Figure 3). The design of the reactor proved to be effective for controlling the ozone doses. There was excellent reproducibility of the results for samples analyzed for colour.

4.4.8 Calibration of Ozone generation system

Ozone generator was calibrated for oxygen flow rate, using a wet test meter. The calculations are given in Appendix VIII.

The volume of the reactor was measured by adding water and by weight / density methods (Appendix VIII). For weight / density method, the same amount of water as added to the reactor, was added to a preweighed beaker and the final weight of the beaker and water was determined. The volume of the cylindrical section of the reactor was measured to be 482.5 mL and 476.8 mL, respectively. Similarly, the volume of spherical section of the reactor was 1083 mL and 1072 mL, respectively. Volume of the reactor as measured by density / weight method was used for calculation purpose.

The amount of ozone diffused into the cylindrical part of the reactor while passing the ozone/oxygen mixture to replace the air occupied in the spherical portion of the reactor was calculated by titrating the KI solution taken in the reactor as described in section 4.4.6. The amount of ozone diffused into the cylinderical part of the reactor was 0.5 mg for an ozone/oxygen concentration of about 4%

(wt/wt) and flow rate of 2 L/min for 10 minutes through the reactor (Appendix VIII).

4.4.9 Ozonation of the Effluent Samples

Ensuring the correct ozone dose, the wastewater sample was placed in the cylindrical section of the reactor, using a long stem funnel, without contaminating the spherical section. The ozone/oxygen mixture was allowed to flow for 5 minutes replacing air from the reactor. The stoppers were closed and the sample was brought in contact with ozone as described for the KI solution.

After 10 minutes of mixing and 20 minutes of reaction time, ozone residual in the reactor was checked by passing nitrogen gas through the reactor and arresting the out coming gases in KI traps. It was found that high ozone demand in the effluent left no ozone residual even at 200 mg O_3/L dose.

The ozonated wastewater was transferred into 1-L beaker for analyses of suspended solids and colour. Part of the ozonated sample was preserved for COD and TOC by acidifying the samples. BOD test was started immediately after completing the ozonation experiments.

5.0 RESULTS

The objectives of the studies were to investigate the improvement in biotreatability of the mill effluent, effect of ozonation on suspended solids, total organic carbon, chemical oxygen demand and the colour removal. It was also noted in the available literature on treatment of pulp mill effluents with ozone, that the location of ozone application was an important factor in the treatment process.

Kraft mill effluent is quite complex in nature due to the presence of high colour, complex compounds and higher chemical oxygen demand, chloride concentration, and toxicity. Presence of toxicity affects the BOD test and is therefore, necessary to reduce these effects, by using well acclimatized microorganisms as well as adopting good experimental techniques to have a uniform basis of comparison of the results. The toxic effects have clearly been noted in the respirometric BOD tests. Presence of complex compounds and chloride contents may effect the COD tests, and also the TOC determinations.

The ozonation study was divided into three broader aspects:

1. characterization of the effluent;
2. ozone system calibration and reactor design; and
3. ozonation of mill effluents.

During characterization stage a well acclimatized population of microorganisms were developed in the laboratory unit and optimum dilutions were determined for BOD tests.

5.1 Characterization of Mill Effluents

For the first set of BOD tests unacclimatized seeds, which were collected during the plant visit, were used. The second set of samples were analysed using acclimatized seed.

As expected, the BOD results showed inhibitory effects for first set of samples, and the rate constant, Ke for secondary effluent was 0.05 / day compared to 0.1 to 0.12 / day obtained using acclimatized seed. Toxic and inhibitory effects were more obvious for bleach effluent which exerted a BOD of 34 mg/L for undiluted sample in respirometer, and dilution improved the BOD to about 200 mg/L (Appendix I).

During the characterization stage major emphasis was placed on optimizing the dilution for BOD test such that the improvement in biotreatability could be measured and comparisons be made between ozonated and unozonated samples. BOD bottles were set up for five different dilutions and BOD_5 vs Dilution was plotted for the effluent samples (Figures 5, 6 and 7). The detailed results are given in Appendix I. 1:100, 1:75 and 1:40 dilutions were selected for bleach, primary and secondary effluents, respectively. The same dilutions were used for setting up the BOD bottles for both ozonated and unozonated samples and thus eliminating the effects of unexpected factors on BOD values.

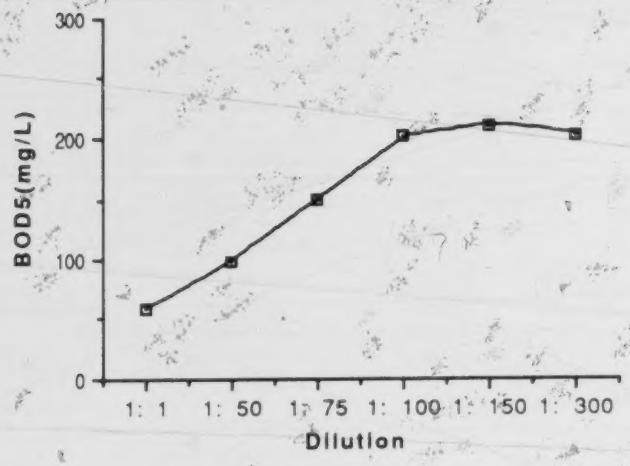

Figure 5. Dilution Optimization for Bleach Effluent

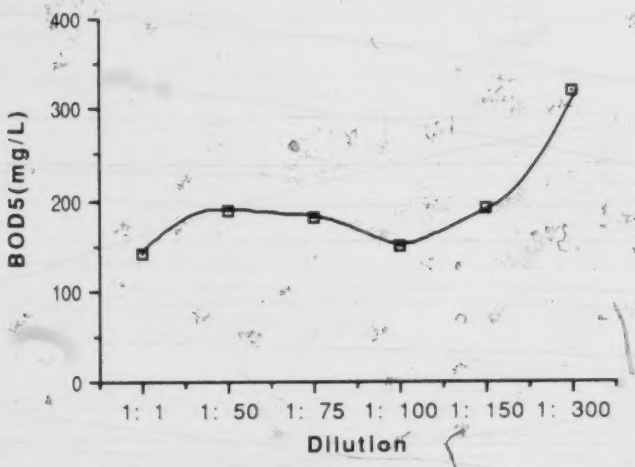

Figure 6. Dilution Optimization for Primary Effluent

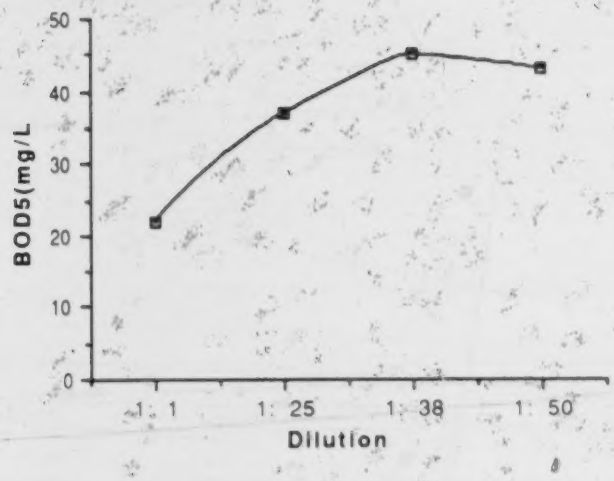

Figure 7. Dilution Optimization for Secondary Effluent

The effluent samples were analyzed for suspended solids, COD, TOC, (filtered and unfiltered), TOX, total phosphate and TKN.

COD/TOC ratio for the effluents was between 2.92 and 3.56, which is characteristic for industrial waste (Eckenfelder, 1966) (Appendix I).

Total suspended solids in the primary effluent were of the order of 100 mg/L which indicate an effective primary treatment at the mill. TSS for secondary effluent were about 90 mg/L but most of them were as volatile suspended solids, and therefore indicate the necessity of secondary clarification in the treatment system (Table 4).

For bleach effluent colour varied between 2,430 and 16,000 units. The large variation in colour was due to grab samples which were collected during different process conditions. Colour for primary and secondary effluent was 1850 and 1770 units, respectively. This supports

the findings that colour is hardly affected during conventional treatment processes.

Table 4. Characteristics of the Pulp Mill Effluent (Actual Range Measured)

PARAMETERS	Bleach Effluent	Primary Effluent	Secondary Effluent
SUS. SOLIDS (mg/L)			
Total	80 to 220	85 to 120	83 to 108
Volatile	60 to 185	50 to 90	66 to 88
BOD5 (mg/L)	200 to 220	180 to 205	26 to 41
BOD20 (mg/L)	360 to 460	270 to 300	56 to 108
T.O.C.(mg/L)			
Filtered	430 to 860	150 to 220	118 to 160
Unfiltered	440 to 860	170 to 240	150 to 200
C.O.D. (mg/L)			
Filtered	990 to 2760	480 to 650	360 to 480
Unfiltered	1170 to 2800	610 to 695	450 to 570
COD/TOC (Unifiltered)	2.7 to 3.3	3.6 to 2.9	3.0 to 2.9
COD/TOC (Filtered)	2.3 to 3.2	3.2 to 3.0	3.1 to 3.0
COLOUR (mg Pt/L)	2430 to 16000	1850	1525 to 1770
T.O.X. (mg/L)	175	60	41
Total Phosphate (mg/L)	0.48	0.62	0.62
Chloride (mg/L)	1138	514	484
Kjeldahl Nitrogen (mg N/l)	40	2.64	2.84

The concentrations of total organic halides were 175 mg/L for bleach effluent, 60 mg/L for primary and 41 mg/L for secondary effluent and, the percentage removal of TOX in aerated lagoon was about 30%.

Samples were also analyzed for total coliform using m-T7 agar to obtain a population. Total coliform in secondary effluent were in the order of 10^6 to 10^7 / 100 mL. The number of coliforms were equally high in primary effluent due to town sewage being combined with primary effluent after the clarifier. Bleach effluent, which was a direct process stream, had no bacterial population. Since the bacterial population in primary and secondary effluents was high, during the studies, the samples were stored at 4° C and the time delay between experimentation and analyses was minimized. Though the first stage was named as characterization, the overall characterization of the effluents was based on the average values of parameters for all the samples analysed during the entire study. The characteristics of the effluent samples are given in Table 4. The effluent, can be characterized as moderately strong.

5.2 Ozonation of Mill effluent

5.2.1 Bleach Effluent

5.2.1.1 Biochemical Oxygen Demand

Ozonation apparently had no effect on 5-day BOD, but the 20-day ozonated samples showed a decrease in BOD values (Table 5). Such results have frequently been reported in earlier studies. The apparently unchanged values of BOD were due to the fact that part of the ozone

reacted with simpler molecules and fulfilled the oxygen demand. At the same time it reacted with complex molecules and made them more biodegradable. As a net result there was no obvious change in BOD for ozonated and unozonated samples. However, ozonation decreased total biodegradable material in the sample.

K_e and L_o values were determined for ozonated and unozonated samples. A very narrow joint confidence region indicated best estimations of those constants (Table 6). K_e for 50 mg/L ozone sample was 0.23 compared to 0.20 for raw sample. However, for 100 mg/L ozone dose both K_e and L_o decreased. The effect of acclimatized and unacclimatized seed was also obvious (Table 6). The K_e values calculated for the BOD results with unacclimatized seed was much lower compared to acclimatized seed.

Table 5. Biochemical Oxygen Demand for Bleach Effluent

Sample	BOD5 (mg/L)	BOD20 (mg/L)
Raw sample	216	358
Oxygen	192	314
50 mg O3/L	199 to 247	313 to 344
100 mg O3/L	188 to 213	312 to 323

Table 6. K_e and L_o for Bleach Effluent

Sample	Ke (1/day)	Lo(mg/L)	Correlation Coefficient
Raw sample	0.08 (Un acclimatized seed)	593	-0.9643
"	0.2	364	-0.785
Oxygen	0.2	317	-0.7857
50 mg O3/L	0.23	315	-0.706
100 mg O3/L	0.21	320	-0.729

5.2.1.2 Chemical Oxygen Demand and Total Organic Carbon

The reduction in COD for bleach effluent was 79 mg/L at an ozone dose of 50 mg/L. For 100 mg/L ozone samples, the decrease in COD was 100 mg/L (Appendix II). The results were analyzed using ANOVA table, and the reduction in COD was found to be significant for ozonated samples. However, the results were not identical for primary and secondary effluents. Ozone effectiveness towards bleach effluent may be due to the fact that the effluent being highly coloured contains large number of molecules with unsaturated bonds. As a result ozone attacked those points readily. There was a good reproducibility of the COD results among the replicates (Appendix II).

For lower ozone doses, TOC remained unchanged as expected. 100 mg/L of ozone reduced the TOC slightly which may be due to the loss of volatile organics as well. TOC and COD samples for filtered

samples were more reliable, since they caused no analytical problems due to incomplete reaction of suspended solids.

5.2.1.3 Colour

Ozone reduced the colour significantly. Since most of the colour is associated with unsaturated bonds in a molecules, ozone has great affinity to attack those sites thus changing the basic characteristics of the molecule. During the ozonation studies, samples were left for few days but no obvious colour reversion was noticed as reported for the effluent treated with lime. For bleach effluent, reduction in colour followed a straightline relationship for the applied ozone doses (Figure 8 and Table 7). However, subsequent experiments with secondary effluent indicated that up to 85% of the colour present in the effluent was readily removed but for higher colour removal significantly high amount of ozone was required. Prat et al. (1988) and Melnyk and Netzer (1975) also reported that 85% of the colour which was readily removed, was due to simple compounds which reacted with ozone more effectively.

Table 7. Colour Removal for Bleach Effluent

Sample	True colour (Pt/Co units)	Colour removal (Pt/Co units)	% Removal
Raw sample	2430	-	
Oxygen	2430	-	
50 mg O3/L	1720	715	29.5
100 mg O3/L	1105	1330	54.5

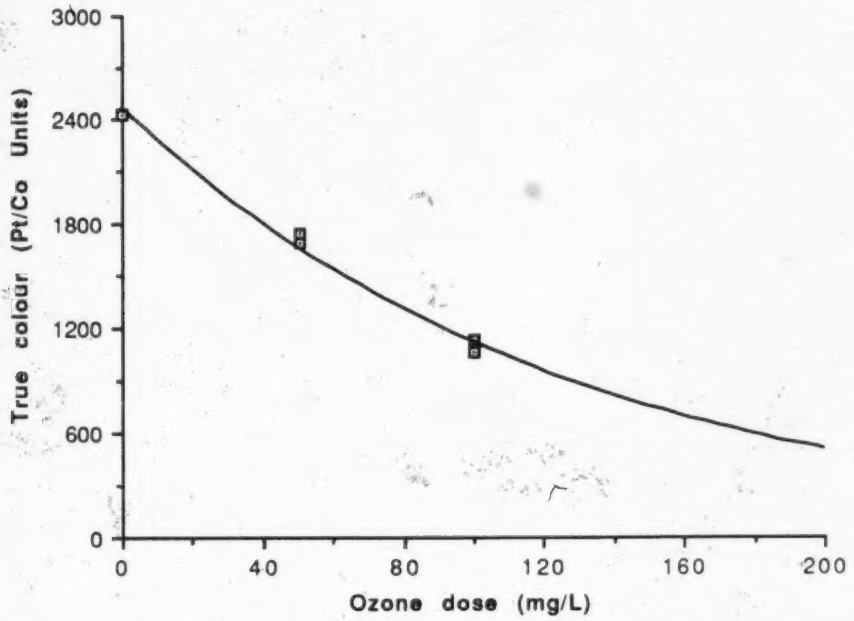

Figure 8. Colour Removal for Bleach Effluent

5.2.1.4 Suspended Solids

Ozone had no statistically significant effect on suspended solids of bleach effluent (Appendix II). The calculated value for 'F' was much

lower than the tabulated value at 95% confidence level and for (2,15) degrees of freedom.

5.2.2 Primary Effluent

A 24-h composite sample of primary effluent was treated with 50 and 100 mg/L of ozone similar to bleach effluent. Two genuine replicate experiments were conducted for each ozone dose and a control experiment was run with pure oxygen. The detailed results are given in Appendix III.

5.2.2.1 Biochemical Oxygen Demand

Similar to bleach effluent, primary effluent apparently showed no significant increase after ozonation (Table 8). The behaviour of the primary effluent sample can be explained on the same lines that for samples with high initial BOD. In those samples most of the ozone is wasted due to its reaction with simple and readily biodegradable compounds and therefore it is not effective at improving the BOD. This behaviour emphasizes the importance of selection of a suitable point of ozone application in the treatment process such that the applied ozone is more effectively used. This point is also important for the selection of ozone contacting / transfer system.

K_e and L_o values calculated for the ozonated samples showed an improvement in biotreatability compared to unozonated samples (Table 15). The joint confidence region plotted indicated a good estimate of parameters.

Table 8. Biochemical Oxygen Demand for Primary Effluent

Sample	BOD5 (mg/L)	BOD20 (mg/L)
Raw sample	205	279
Oxygen	174	308
50 mg O3/L	170 to 179	252 to 285
100 mg O3/L	178 to 182	267

Table 9. K_e and L_o for Primary Effluent

Sample	Ke (1/day)	Lo (mg/l)	Correlation Coefficient
Raw sample	0.19	292	-0.7937
"	0.25	264	-0.7776
Oxygen	0.16	298	-0.8918
50 mg O3/L	0.23	254	-0.8193
100 mg O3/L	0.23	260	-0.8162

5.2.2.2 Colour

Compared to bleach effluent , colour was more readily reduced for lower ozone dose. 50 mg/L of ozone reduced the colour of primary effluent by 850 units. Similar ozone dose for bleach effluent reduced the colour by 715 unit. However, for 100 mg/l ozone dose, the colour reduction was identical for both the effluents (Table 10 and Figure 9).

Table 10. Colour Removal for Primary Effluent

Sample	True Colour (Pt/Co units)	Colour Removal (Pt/Co units)	% Removal
Raw sample	1850	-	
Oxygen	1750	-	
50 mg O3/L	1000	850	46
100 mg O3/L	510	1345	73

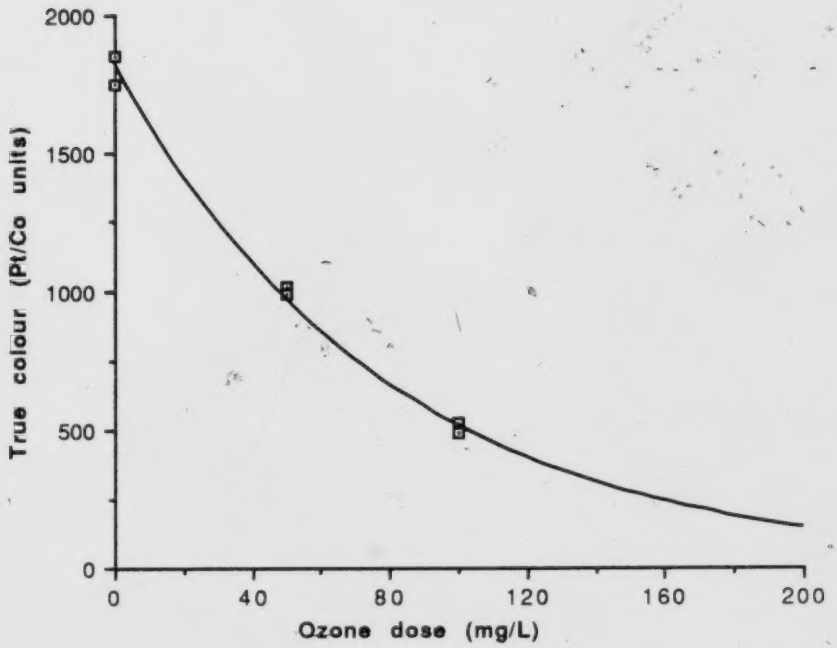

Figure 9. Colour Removal for Primary Effluent

5.2.2.3 Chemical Oxygen Demand and Total Organic Carbon

COD for ozonated samples was lower than unozonated samples. The decrease in COD was significant at 95% confidence level. The calculted value for F was 6.63 compared to tabulated value of $F_{95}(2,15)$ of 3.68.

The decrease for primary effluent was not as much as bleach effluent. Bleach effluent being a highly coloured effluent had more unsaturated bonds and provided more sites where ozone could react. With primary effluent which has a large variety of compounds, part of the applied ozone might have had additional reaction and reacted in different ways. This might be the reason, a clear relationship could not be established between applied ozone doses and its effect on COD (Appendix III).

5.2.2.4 Suspended Solids

Lower ozone dose did not reduce the suspended solids significantly, but for 100 mg./L ozone dose, reduction in suspended solids was noticeable (Appendix III).

5.2.3 Secondary Effluent

Similar to bleach and primary effluent, secondary effluent for the first set of experiment was treated with 50 and 100 mg/L of ozone. BOD results showed significant improvement for the ozonated samples (Table 11). To confirm the results, four more replicate experiments were conducted. All the four experiments showed a similar increase in the BOD values for the ozonated samples. Two more samples of secondary effluent were treated with 150 mg/L of

ozone dose and one experiment was conducted for 200 mg/L of ozone dose to establish the pattern of improvement for higher ozone doses. All the samples were analyzed for COD, TOC, suspended solids and colour. The detailed results are given in Appendices IV, V, VI and VII).

Table 11. Biochemical Oxygen Demand for Secondary Effluent

Sample	BOD5 (mg/L)	BOD20 (mg/L)
Raw sample	26 to 41	56 to 108
Oxygen	34 to 39	62 to 116
50 mg O3/L	45 to 59	78 to 120
100 mg O3/L	50 to 71	102 to 148
150 mg O3/lL	73 to 81	123 to 140
200 mg O3/L	90	138

5.2.3.1 Biochemical Oxygen Demand

Samples of ozonated and unozonated effluent were set up for BOD test in identical manner and titrated to estimate BOD for 1,2,3,4,5,7,10 and 20 days. K_e and L_o values were calculated and joint confidence region was plotted to check the accuracy of parameter estimation.

Six replicate experiments were conducted for 50 and 100 mg/L ozone doses for the purposes of statistical calculations. The statistical calculations are given in Appendix IX. The calculated values for "t"

were higher than table values, therefore the H_o(null hypothesis) is incorrect and there was a significant improvement in BOD_5 of the secondary effluent with ozonation (Appendix IX). The results were also analyzed using ANOVA table which confirmed the significant improvement in BOD_5 for ozonated samples.

Table 12. K_o and L_o for Secondary Effluent

Sample	Ke (1/day)	Lo (mg/L)	Correlation Coefficient
Raw sample	0.05	209	-0.9918
	(Unacclimated seed)		
	0.15	63	-0.8633
	0.1	70	-0.9184
	0.11	66	-0.8987
	0.13	70	-0.9041
Oxygen	0.13	70	-0.8831
	0.11	74	-0.9333
50 mg O3/L	0.2	82	-0.8382
	0.24	86	-0.7012
	0.16	87	-0.8073
	0.19	83	-0.8059
	0.19	82	-0.6905
	0.19	77	-0.7006
	0.15	88	-0.8368
	0.17	83	-0.7383
100 mg O3/L	0.24	99	-0.8065
	0.19	111	-0.7322
	0.15	116	-0.8277
	0.16	115	-0.8402
	0.16	113	-0.8696
	0.19	104	-0.845
	0.15	114	-0.7751
	0.17	107	-0.8159
	0.19	114	-0.7115
	0.21	104	-0.6835
150 mg O3/L	0.15	126	-0.7929

5.2.3.2 Colour

Colour was more effectively removed from secondary effluent. For 50 mg/L ozone dose the reduction was about 1000 units compared to 715 and 850 unit for the bleach and primary effluent respectively. However, for higher ozone doses the reduction tapered off (Tables 13 and Figure 10).

Table 13. Colour Removal for Secondary Effluent

Sample	True Colour (Pt/Co Units)	Colour Removal (Pt/Co Units)	% Removal
Raw Sample	1525 to 1770		
Oxygen	1550 to 1820		
50 mg O3/L	500 to 700	950 to 1060	58 to 67
100 mg O3/L	250 to 370	1205 to 1470	77 to 85
150 mg O3/L	170 to 215	1360 to 1600	86 to 90
200 mg O3/L	185	1585	90

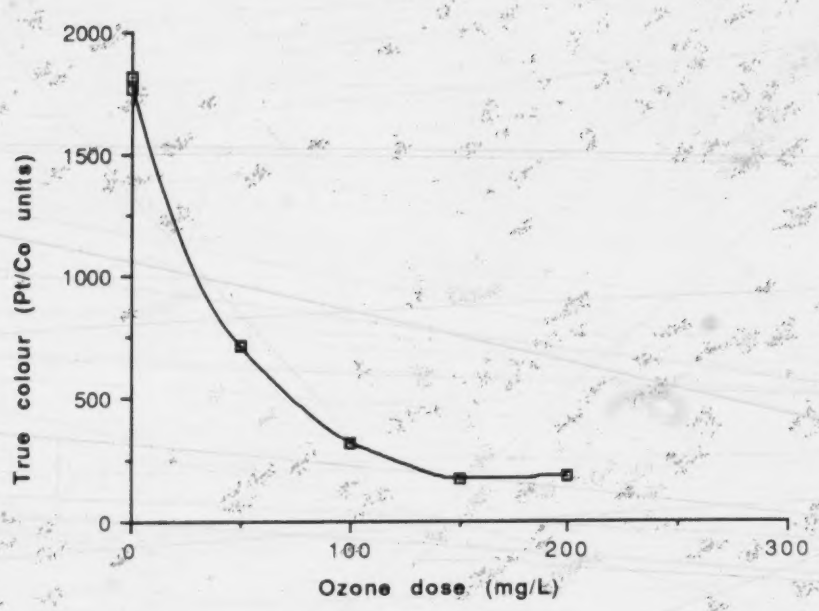

Figure 10. Colour Removal for Secondary Effluent

5.2.3.3 Suspended Solids

Reduction in suspended solids was less in comparison to the improvement in BOD or colour reduction (Appendices IV,V,VI and VII). 50 mg/L of ozone had no significant effect on TSS and VSS, but the reduction in suspended solids for 100 mg/L ozone dose was found to be significant by 't' test. The statistical calculations are given in Appendix IX. Analysis of variance, performed for no ozone dose, 50 mg/L and 100 mg/L ozone doses indicated a small but significant reduction in total suspended solids of secondary effluent. The calculated value of 'F' was 5.76 compared to tabulated value of $F_{95}(2,15)$ as 3.68.

5.2.3.4 Chemical Oxygen Demand

Reduction in COD showed no pattern which could be related with applied ozone doses (Appendices IV,V,VI and VII). Statistically there was no significant effect of ozonation on COD of secondary effluent. The mechanism of ozone effect on COD, as discussed before, seemed to be complex and is not a simple addition reaction. The effluent also had large amounts of complex organics, which might not be completely oxidized during COD test.

6.0 DISCUSSION

The three basic objectives of ozonation study were: to investigate the improvements in biotreatability, over all treatability of mill effluents and identify the suitable location of ozone application.

As described in introduction (Section 1.0) and literature review (Section 2.0), the conventional methods of effluent treatment were not sufficient to achieve the high standards of treatment. Ozone is an attractive alternative to treat the effluent more effectively.

The available literature on this subject supports ozone to be effective for the removal of colour, odour, surface active and foaming compounds; reduction in COD, improvement in biotreatability of the effluent, and degradation of organochlorines and dioxins. A couple of studies also indicated that the ozonation process might be economical for the removal of colour from the effluent. The points missing in the available literature are:

1. most of the studies have been conducted with single effluent stream (i.e. primary effluent, secondary effluent or bleach effluent);
2. it is difficult to correlate the results from different studies, since the effluents are not from the same source and their characteristics vary considerably;
3. ozone doses vary from 10 mg/L to 550 mg/L;
4. reactors, which have pronounced effect on the overall efficiency of ozonation process, were different for all the studies, therefore

the efficiency obtained for one reactor need not be same for another system.

The studies were designed to investigate the effect of ozone on the characteristics of pulp mill effluent by controlling the ozone dose. The available literature also indicated the significance of proper location of ozone application. The first objective was achieved by designing a batch reactor in which a better control on ozone dose was achieved. For the second objective, samples were collected from three different locations at the mill.

The reactor was found to be effective with respect to ozone doses (Figure 3). A maximum variation of 5 mg ozone was achieved among the replicate experiments for all ozone doses. The accuracy of the ozone doses was evident with the potassium iodide titration method and from the colour reduction for replicate samples for all the effluents, which was found to be consistent.

During the ozone determination the level of potassium iodide solution in the 6 mm connecting glass joint was noticed to be critical with respect to ozone diffusion into the potassium iodide solution (i.e. the cylindrical section of the reactor). When the potassium solution was filled well up in the connecting glass tube, the small surface area was excellent at reducing the ozone diffusion into the potassium iodide solution as the ozone / oxygen mixture was filling the reactor. Under the above conditions the amount of ozone transferred into the potassium iodide solution was as low as 0.5 mg. The amount of ozone

diffused into the effluent, therefore, was insignificant compared to the applied ozone doses ranging between 50 and 200 mg/L.

A well acclimatized seed are important to have a better estimate of BOD for industrial waste. Most often for industrial waste it is necessary to add a population of microorganisms capable of oxidizing the biodegradable organic matter in the sample. The use of non-acclimated biological seed in the BOD test is probably the factor most commonly responsible for erroneous BOD results (Eckenfelder, 1966). This is particularly true when considering complex industrial wastes. The initial seed can be obtained from the waste treatment facility treating similar wastewater, if possible, otherwise surface water (preferably 3 to 8 km below the discharge) receiving wastewater discharges contain satisfactory microbial population. It is best to acclimatize the biological culture in a continuous reactor although fill and draw batch units are frequently used (Eckenfelder, 1966). The diluted wastewater is fed to the initial microbial seed, increasing the wastewater strength over a period of time. Once the continuous or batch system has been subjected to the undiluted waste, the mixed contents should be aerated until the organic removal by the seed organism reaches a maximum level. Once this has occurred the system can be considered acclimated. For domestic-industrial waste the time required may be about a week. However, for industrial waste containing high concentrations of complex organic compounds, it may take several weeks (Eckenfelder, 1966).

The presence of toxic materials in the wastewater sample may have a bio-toxic or bio-static effect on the seed organisms (Eckenfelder, 1966). This effect is evidenced by the BOD values which increase with sample dilutions. It is therefore necessary to predetermine the dilution value above which the biochemical oxygen demand is consistent. If toxicity is due to heavy metals, their effect can be eliminated by chelation (Eckenfelder, 1966).

In the initial stage of study, seed were collected from the pulp mill laboratory and set up for acclimatization purpose. The first set of samples were analyzed using unacclimatized seed and rest of the BOD test during the entire study were conducted using well acclimatized seed. The BOD values obtained for these two set of tests pointed out toxic and inhibitory effects of the mill effluents. The toxic effects were more significant for bleach stream which exerted a BOD of 34 mg/L with unacclimatized seed compared to 200 with acclimatized microorganisms. K_e value for for secondary effluent was 0.05/day with unacclimatized seeds compared to 0.1 to 0.12 with acclimatized seed. Inhibitory effect were reduced by selecting a suitable dilution for BOD tests for each effluent.

During the appropriate dilutions determinations for the three samples, it was noted that for 20-days BOD the microorganisms were very well acclimated, and the BOD for different dilutions was identical.

Oxidation of nitrogenous materials adds to the BOD values which are generally considered as a measure of carbonaceous fraction of the sample.

The measurement of carbonaceous oxygen demand can be done in two ways: by retarding nitrification in the BOD test by adding inhibitors, or by allowing nitrification to take place and subtracting its demand from the overall results (Eckenfelder, 1966). It should be recognized that nitrification occurs in most of the effluents which have undergone a biological treatment, and exerts an oxygen demand on the receiving waters. Therefore, nitrogenous oxygen demand should be considered as part of the total oxygen demand on the receiving environment. For the BOD test, Allythiourea at a concentration of 10 mg/L, as recommended by Young (1981) was added to the dilutioin water. The BOD values, therefore, represent Carbonaceous Biochemical Oxygen Demand (CBOD).

The concentrations of total organic halides were 175 mg/L for bleach effluent, 60 mg/L for primary and 41 mg/L for secondary effluent and, the percentage removal of TOX in aerated lagoon was about 30% (Table 4). The measured removal of TOX was close to the value reported by Bryant et al. (1987). It was planned to study the effect of ozonation on the TOX of the mill effluents, but the inconsistent results of TOX obtained in the subsequent samples due to operational problems with the Organic Halides Analyzer, resulted in the effort being abondoned. The analysis of the samples for TOX was limited to one sample for the purpose of characterization. It would be interesting if the effects of ozonation on organic halides had been determined in conjunction with the ultrafiltration. The results could have given the insight on the ozonation effects which were expected to degrade the

larger molecules into simpler forms. These simpler molecules formed are reduced during subsequent biological treatment. The fate of the organohalides have always been questionable in the receiving waters. It has been identified that it is the lower molecular compounds which are more toxic to the aquatic organisms than the larger molecules (Bonsor et al. 1988). However, it is also reported that the larger molecules, once discharged into the receiving waters start slowly degrading and form lower molecular weight compounds, which would have more damaging effects on the receiving water. In a situation where ozone could be used as an intermediate stage of treatment during the biological treatment process, it would react with complex compounds forming other molecules that might be relatively toxic but more biodegradable. The removal of these compounds would be quite possible with a better acclimated bacterial population in the biological treatment system.

Experiments were run in duplicate for bleach and primary effluent. The improvement in biotreatability and BOD was insignificant for these samples. Secondary effluent showed an improvement in biotreatability as well as an increase in the total quantity of biodegradable organics. For secondary effluent six replicate experiments were conducted to check the statistical significance of the results. Two more experiments were conducted for 150 mg/L and one experiment was run for 200 mg/L ozone dose to investigate the effects of higher ozone doses on the effluent characteristics.

6.1 Biochemical Oxygen Demand

Ozonation of bleach effluent (BOD_5=216 mg/L) resulted in improvement in biotreatability i.e. higher K_e values (Table 14, Figure 11), but the total quantity of biodegradable material decreased with ozonation both for 50 and 100 mg O_3/L doses. The increase in K_e value for 50 mg/L was higher and the decrease in L_o was lower compare to 100 mg O_3/L dose.

Table 14. Ke and Lo values for Bleach, Primary and Secondary Effluents

SAMPLE	Ke(1/day)	Lo(mg/L)
BLEACH EFFLUENT		
Raw sample	0.20	364
Oxygenated sample	0.20	317
50 mg O3/L dose	0.23	315
100 mg O3/L dose	0.21	320
PRIMARY EFFLUENT		
Raw sample	0.19 to 0.25	264 to 292
Oxygenated sample	0.16	298
50 mg O3/L dose	0.23	254
100 mg O3/L dose	0.23	260
SECONDARY EFFLUENT		
Raw sample	0.1 to 0.15	60 to 80
Oxygenated sample	0.1 to 0.13	65 to 80
50 mg O3/L dose	0.15 to 0.24	80 to 90
100 mg O3/L dose	0.15 to 0.24	100 to 120
150 mg O3/L dose	0.15	126

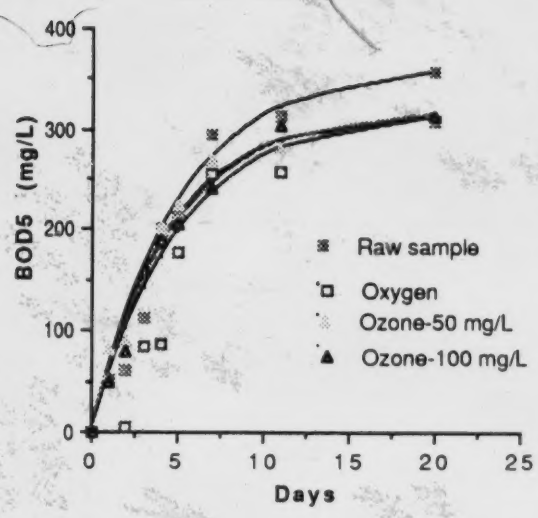

Figure 11. Biochemical Oxygen Demand for Bleach Effluent

Similarly for primary effluent (BOD_5=205 mg/L) the K_e values decreased slightly with ozonation, whereas the L_o remained same (Table 14 and Figure 12).

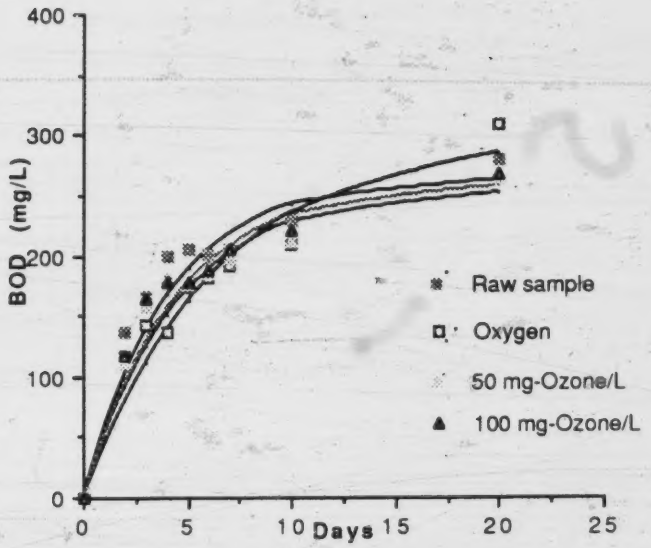

Figure 12. Biochemical Oxygen Demand for Primary Effluent

The apparent ineffectiveness of ozone for the effluents having high initial BOD had most frequently been reported for pulp mill effluents. This tendency can be explained when we look at the TOC values. It was observed that for all the ozone doses there was a small decrease in the TOC values i.e. some of the simple compounds were completely oxidized and removed from the effluent. More complex compounds reacted with ozone and the resulted simple compounds were available for biodegradation, as a result the overall effect of ozonation was completely masked. Similar results have been reported by Smith and Furgason (1974) (Figure 13).

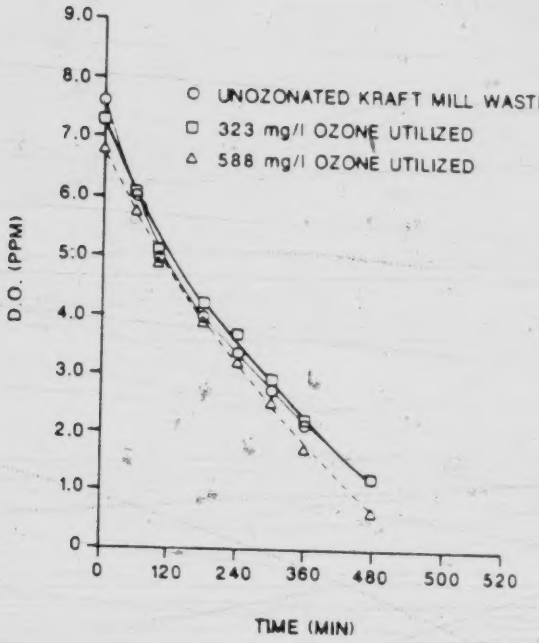

Figure . Oxygen Uptake Study (Adapted from Smith and Furgason 1976)

In comparison to bleach and primary effluent, secondary effluent (BOD_5=26 to 41 mg/L) showed a significant improvement in K_e and L_o values (Table 14, Figures 14).

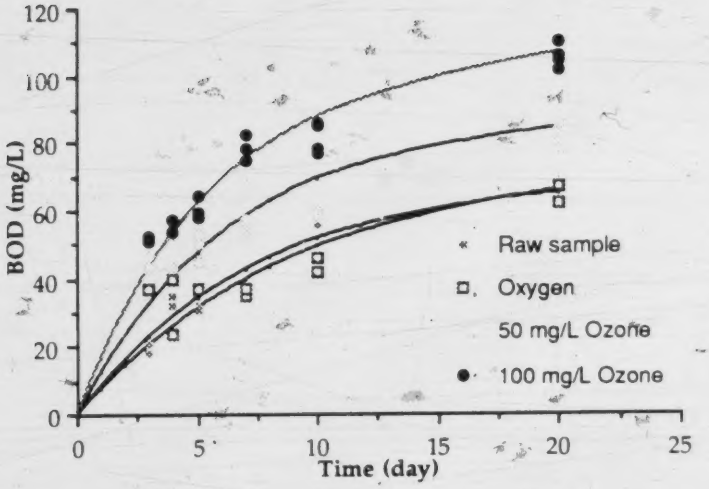

Figure 14. Biochemical Oxygen Demand for Secondary Effluent

Between 65% to 100% improvement in BOD was noted for 50 and 100 mg/L of ozone doses. Both 5-day and 20-day BOD increased with ozonation. The increase in BOD for secondary effluent with ozonation supports the theory that for effluents with high initial BOD part of the ozone reacted with simple compounds and fulfilled their oxygen demand. The other part of ozone reacted with complex molecules, which were not readily biodegradable, and changed them into a simpler form. However, with secondary effluent which had already 80 to 90% of simple compounds removed during biological treatment, and had greater proportion of complex molecules, ozone was more effective towards them. Sozanska and Sozanski (1989) reported a threshold limit of 23 mg/L of initial BOD for an increase or

decrease in the BOD for ozonated samples. However, that limit is dependent on the proportion of complex molecules present in the sample, and also the ozone contacting device. If the ozone molecules are brought in contact more rapidly with the effluent molecules there is a possibility of ozone reacting with a larger number of molecules than reacting with a single molecules to greater extent.

The rate of BOD removal (or effect on BOD) is a function of ozone concentration in the effluent. Reaction of ozone for the effect on BOD can be written as:

$$-dr / dt = k\, C_{BOD}\, C_{O3} \qquad (20)$$

As ozone concentration reduced to zero in the effluent, the rection ceases. Ozonation of primary and bleach effluent resulted in no significant increase in BOD, whereas for secondary effluent, ozonation improved BOD. This phenomenon indicated that there were competing reactions occuring with ozone. As a result ozone was much quickly consumed in primary and bleach effluents, before it could react with complex molecules and improve the BOD.

Secondary effluent, which already had undergone biological treatment, had complex compounds with low BOD_5; ozone attacked these compounds effectively and converted them into simpler forms which were subsequently biodegraded at a faster rate.

Secondary samples with an initial BOD_5 between 26 to 41 mg/L showed an average increase in BOD_5 of 65% and 100% for 50 and 100 mg O_3/L doses respectively. The relatively improvement in BOD_5 for an increase in ozone dose from 100 to 150 mg O_3/L was smaller than

the increase from 50 to 100 mg O_3/L dose. Similarly the increase in BOD_5 for an ozone dose increased from 150 to 200 mg O_3/L was smaller than that for 100 to 150 mg O_3/L. It was believed that up to 100 mg O_3/L dose ozone had more opportunity to react with rather complex compounds, while a further increase in dose resulted in ozone reacting with some of the already degraded compounds along with complex molecules. As a result the effectiveness of ozone was less (Table 15).

K_e and L_o values which represent the biotreatability and total amount of biodegradable material in an effluent, increased with ozonation. The newly formed molecules in the effluent after reacting with ozone, were consumed by microorganisms at about twice the rate of raw sample.

Table 15. Improvement in BOD for Various Ozone Doses

SAMPLE	Bleach Effluent		Primary Effluent		Secondary Effluent	
	BOD5 (mg/L)	BOD20 (mg/L)	BOD5 (mg/L)	BOD20 (mg/L)	BOD5 (mg/L)	BOD20 (mg/L)
Raw Sample	216	358	205	279	26-41	56-108
Oxygen-dose	192	314	174	308	34 to 39	62 -116
50 mg O3/L	199-247	313-344	170-179	252-285	46-59	78-120
100 mg O3/L	188-213	312-323	178-182	267	50-71	102-148
150 mg O3/L	-	-	-	-	73-81	123-140
200 mg O3/L	-	-	-	-	90	138

A slight bump in the BOD curves was noticed for secondary effluent even though the total kjeldahl nitrogen was between 3 to 5 mg-N/L. It was not believed that nitrification played any role in higher values of BOD for ozonated samples due to the fact that nitrogen inhibitor was added for BOD test, and unless NH_4 are broken off large molecules, it does not exert oxygen demand. Since the ozonated and unozonated samples were run in pairs, even if there could have been some nitrification the overall effect would be neutralized, as the difference in BOD values of ozonated and unozonated samples were taken under identical conditions.

The bumps in BOD curve can be expected for pulp mill effluents which have a range of simple alcohols and sugars to complex form of lignin compounds. Raabe(1968) identified three groups of compounds in pulp mill effluent with distinct differences in the rate of biodegradation (Figure 15).

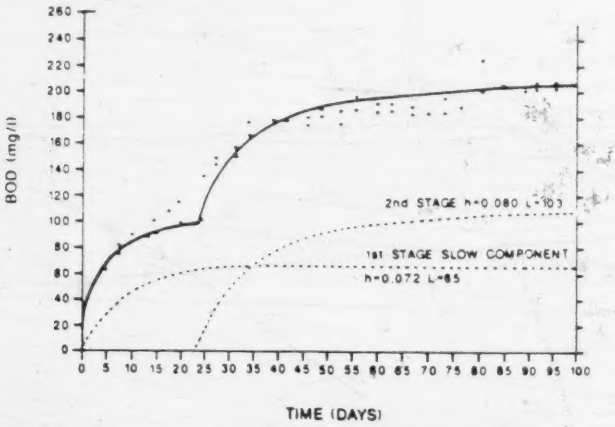

Figure 15. Long-term BOD Over 100 Day Period for Pulp Mill Effluent (Adapted from Raabe, 1968)

Initially it was planned to set-up the respirometer along with BOD bottles to study the oxygen uptake rate for undiluted samples. However, even with acclimatized seeds the oxygen uptake rate in respirometer were quite erratic and showed signs of inhibition effects. When the respirometer was checked for gas leaks, the increase in the micrometer readings after increasing the temperature by 0.3° C, was (±) 5 microlitre, which is within the limits of accuracy of the equipment (Appendix I). A significant difference was noted between the BOD values determined by bottle method and that of respirometer. Therefore, at a later stage it was decided to collect extensive data using 300 mL BOD bottle method. The results obtained subsequently had good reproducibility for replicates.

"t" statistics calculated for paired experiments indicated that pure oxygen had no significant effect on treatability. The results obtained for the oxygenated samples were similar to the raw samples (Appendix IX).

On the other hand there was a significant improvement in BOD_5 for 50 and 100 mg O_3/L doses. The tabulated values of 't' at 95% and 99.9% were 2.015 and 5.893; whereas the calculated values were 5.331 and 8.265 for 50 and 100 mg O_3/L doses respectively. Analysis of variance also indicated a highly significant improvement in BOD after ozonation. Residuals were plotted to confirm the assumptions of constant variance and normal distribution for the data.

The BOD equation was solved for K_e and L_o using a computer program for the solution of non-linear equations. The joint confidence

region was plotted to check the reliability of these parameters. The smaller a joint confidence the better the estimates for the parameters; while a large and irregular joint confidence would mean the calculated values of the parameters are not reliable (Berthouex et al., 1971).

The BOD rate constant K_e for raw sample was between 0.1 to 0.15; and the improved values for 50 and 100 mg O_3/L doses were between 0.15 to 0.24 and 0.15 to 0.24/d respectively (Table 14). The best estimates of K_e were 0.17/d for 50 mg O_3/L, 0.21 for 100 mg O_3/L (Table 16). Melnyk and Netzer (1977) reported that after ozonation there was an overall increase in biotreatable organics, but the resulting molecules degraded at a slower rate. In the present studies this trend was observed at higher ozone doses, but all the ozone doses improved the biotreatability in comparison to unozonated sample.

The Ke and Lo value for raw sample were plotted on the grids that of 50 mg/L and 100 mg/L ozone doses (Figures 16 and 17). Since the calculated value of raw sample did not fall within the JCR of ozonated samples, it indicated that there is a significant difference in the biotreatability of ozonated and unozonated samples.

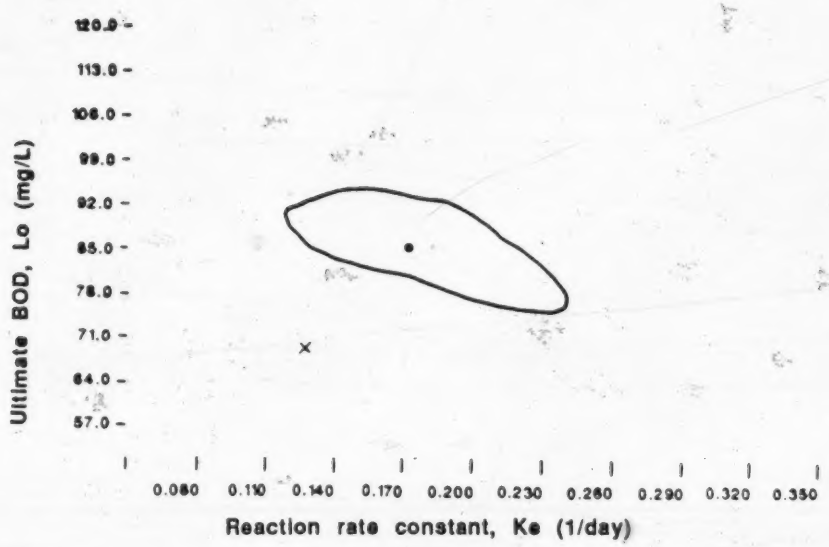

Figure 16. Appriximate 95% Joint Confidence Region for 50 mg O3/L Dose for Secondary Effluent

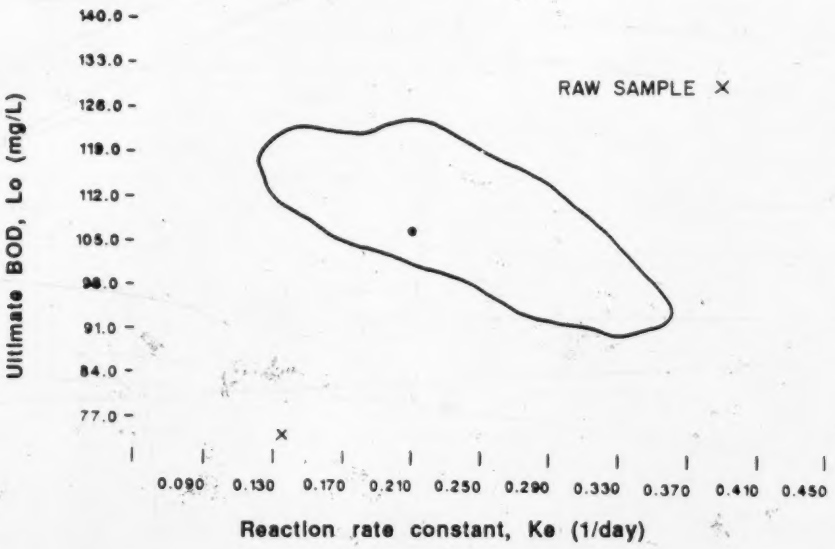

Figure 17. Approximate 95% Joint Confidence Region for 100 mg O3/L Dose for Secondary Effluent

Table 16. K_e and L_o of the Plotted JCR for Secondary Effluent

Sample	Ke (1/day)	Lo (mg/L)	Correlation Coefficient
Raw Sample	0.13	70	-0.9041
50 mg O3/L	0.17	83	-0.7383
100 mg O3/L	0.21	104	-0.6835

6.2 Colour Removal

Ozone was extremely effective for the reduction of colour from pulp mill effluents. Irrespective of the effluent streams, colour removal was evident for all ozone doses. Ozone reduced the colour by altering the molecular structure of the compounds; with no by products generated requiring separate handling.

The effectiveness of ozone increased from bleach<primary effluent<secondary effluent. It seemed that the colour causing molecules in bleach stream were relatively complex in nature and as a result the colour removal was noted to be smaller compare to primary and secondary effluents. It was also noted that biological treatment had a significant effect on the colour causing molecules and made them more reactive with ozone. It is also possible that, biological treatment reduced the competing colour causing molecules in the secondary

effluent. As a results, ozone was more effective with secondary effluent.

Reaction of ozone for colour removal can be given as:

$$-dr / dt = k\, C_{colour}\, C_{O3} \qquad (21)$$

For low ozone dose and high initial colour concentration, the rate of colour removal will become a pseudo-first order reaction and depends on the concentration of ozone in the effluent. As ozone is consumed in the effluent, decolourization reaction ceases. Thus colour removal is a function of ozone stability in the effluent as well the competative reactions which occur along with decolourization. Ozone being selective, reacts with more reactive species in the effluent. These species may be organic or inorganic in nature. The competing reactions were evident during the colour removal for bleach, primary and secondary effluents. It looked like bleach effluent had more reactive species, as a result part of the ozone was consumed by those molecules. The colour causing molecules had to compete with them to react with ozone. The colour removal for bleach effluent was 750 units for an applied ozone dose of 50 mg/L. Primary effluent which had relatively less non colour species, was decolourized to higher extent. The colour removal was 840 APHA units. Secondary effluent which already had undergone biological treatment, the more reactive species had been removed during the biological treatment and therefore, had smaller number of species which were competing with colour causing

molecules for reacting with ozone. This resulted in higher colour reduction for secondary effluent.

At higher ozone doses, the decolourization reaction might become a second order reaction. There was enough ozone present in the effluent to satisfy the demand of more reactive species and react with colour causing molecules. As a result, ozone was equally effective for bleach, primary and secondary effluents at 100 mg/L ozone dose.

The colour reduction for all three wastewater streams was between 680 to 1095 unit for the 50 mg/L ozone dose, whereas for the 100 mg/L ozone dose the corresponding reduction was between 1300 to 1470 units (Table 17).

Table 17. Colour Reduction (Platinum Cobalt Units) for Mill Effluents

Ozone dose (mg/L)	Bleach Effluent			Pond Influent			Secondary Effluent		
	X	Range	% reduction	X	Range	% reduction	X	Range	% reduction
50	715	680 to 745	28 to 31	850	840 to 860	45 to 47	1025	950 to 1060	58 to 67
100	1330	1330 to 1360	53 to 56	1345	1325 to 1360	80 to 84	1350	1205 to 1470	77 to 85
150	-	-	-	-	-	-	1480	1360 to 1600	86 to 90
200	-	-	-	-	-	-	1585	1585	90

The wide spread in colour reduction for lower ozone dose and smaller spread at higher dose might be interpreted that, for higher ozone doses the ozone is equally reactive with all the effluents (Figure 18).

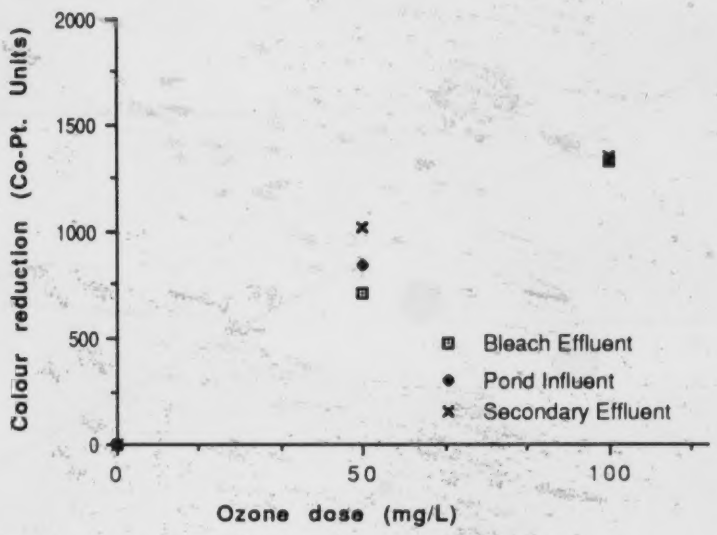

Figure 18. Colour Reduction Spread for Mill Effluents

Secondary effluent which was examined in detail had an initial colour between 1525 to 1770 units. The reduction in colour for 50 mg O_3/L was 58 to 67%; for 100 mg O_3/L the corresponding reduction was 77 to 85%. But further increase in ozone doses resulted a small reduction in the total colour units (Table 17). This exponential behaviour supported the assumption that there were at least two groups of compounds responsible for total colour in the mill effluents with different reactivity towards ozone (Figure 19). The first group of compounds, which was dominant and constituted up to 85% of the

total colour in secondary effluent, reacted readily. The second group of compounds which were more resistant reacted relatively slowly with ozone.

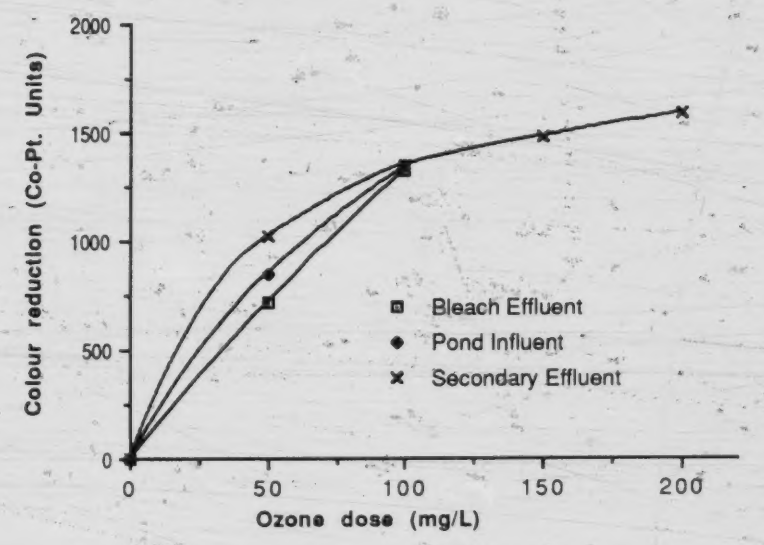

Figure 19. Colour Removal for Mill Effluents

Ng et al. (1978) suggested a relationship between applied ozone dose and colour reduction for kraft mill effluent which is given as Equation (2).

The measured colour removal for bleach effluent was 715 and 1330 units for an applied ozone dose of 50 and 100 mg/L respectively. The calculated reduction from the above relationship was 730 and 1200 units.

6.3 Chemical Oxygen Demand and Total Organic Carbon

The chemical oxygen demand is a measure of the organic matter in the sample which can be oxidized by strong oxidizing agents such as permanganate and dichromate in acid solution. Theoretically it would be expected that BOD of a wastewater to be equal to the COD, but it is not true for various reasons (Eckenfelder, 1966).

1. Many organic compounds which are dichromate oxidizable are not biochemically oxidizable. This aspect is very common for industrial wastewaters.
2. The BOD results may be affected by lack of seed acclimation and toxic effects, giving low readings. The COD results are independent of these variables.
3. Chlorides are oxidized by dichromate, provision should be made to eliminate this interference (Eckenfelder, 1966). High COD values will occur by the oxidation of chlorides by dichromate.

This interference is eliminated by adding $HgSO_4$ (10:1 ratio of $HgSO_4$:Cl) to the reaction mixture.

It was suspected earlier that the concentration of chloride might be high in the samples due to chlorine bleaching operation, however, the chloride contents were measured between 300 to 600 mg chloride/ L of the samples. At these chloride concentrations 0.4 g $HgSO_4$ was enough to reduce the interference of chloride on COD test. Three blank test, under identical conditions, were conducted for each set of COD determinations.

Unlike BOD and colour reduction, the trend in COD and TOC was not clear, and it was hard to draw any conclusions from the results. Theoretically for 100 mg O_3/L dose, the drop in COD value should have been 100 mg, if all the ozone reacted. The reaction did not seem to be only addition reaction. On the other hand ozone reacted with some of the molecules and oxidized them completely, resulting in a loss of carbon as well as oxygen. These factors might have affected the reduction in COD which was not reproducible for replicate experimental runs.

To establish the analytical technique, standard COD analysis were done adding 500 mg Cl/L which corresponded to the level of chlorides present in primary effluent and secondary effluent. The results had a standard deviation of 20 mg/L and 36 mg/L respectively at 250 mg/L and 500 mg/L COD levels. The corresponding coefficient of variance were 7% for both the analyses. The above variations were within the levels given by Standard Methods(APHA, AWWA, WPCF, 1985) (Appendix I).

TOC reduction ranged between 10 to 20 mg/L for 50 to 200 mg/L ozone doses (Appendix X). Similar to COD there was no clear correlation for TOC reduction at various ozone doses. Even though the reduction in TOC was small and statistically insignificant, the decrease was very consistent for all the ozone doses, and could not be ignored.

The relationship between COD and TOC values might not be clear for the following reasons:

1. some of the fibrous material present in the effluents might not be oxidized during COD and TOC determination of unozonated samples, but might be more reactive after ozonation, as a result the expected drop in COD was not noticed,
2. simultaneous decrease in TOC for ozonated samples; and
3. unexplainable interference in COD analyses.

On a broad basis, it could be concluded that ozone application decreased the chemical oxygen demand and total organic carbon of pulp mill effluents.

COD/TOC ratio for the effluent samples was about 3 which is characteristic for industrial waste (Appendix X). The ratio did not change significantly for ozonated and unozonated samples. This might be due to the fact that for ozonated samples, there was a decrease in TOC along with COD.

6.4 Suspended Solids

Effect of ozone on suspended solids of the mill effluents was unclear similar to COD and TOC (Appendix X). There was no significant decrease in total suspended for 50 mg O_3/L. The decrease in TSS was significant at 100 mg/L ozone dose. The decrease was 12% for secondary effluent, 6% for bleach effluent and 24% for primary effluent. For bleach and primary effluent samples, the experiments for ozone doses were conducted in duplicate, and for secondary effluent sample, six replicate experiments were carried out.

7.0 CONCLUSIONS

1. Ozonation of bleach effluent (BOD_5=216 mg/L) resulted in slight improvement in biotreatability (i.e. K_e factor) but the total quantity of biodegradable organics decreased as well. No statistically significant improvement in BOD_5 was noted.
2. Primary effluent (BOD_5=205 mg/L) sample showed a slight decrease in both K_e factor and total amount of biodegradable material. However, no significant effect on BOD_5.
3. Secondary samples with initial BOD_5 in the range of 26 to 41 mg/L showed a significant improvements both in biotreatability as well as the total quantity amount of biodegradable organics. The average improvement in BOD_5 for secondary effluent was 65% and 100% for an ozone doses of 50 and 100 mg/L respectively.
4. The most significant improvement with ozonation was colour removal. The effectiveness of ozone for removing colour was highest when the effluent had undergone biological treatment. For secondary effluent the average reduction in colour was 62% for 50 mg O_3/L dose and 82% for 100 mg O_3/L.

5. Unlike BOD and colour, a clear relationship could not be established for the reduction in suspended solids, COD and TOC for various ozone doses.

8.0 RECOMMENDATIONS

The results indicated that ozonation was an effective treatment for the overall improvement in treatability of pulp mill effluent. Since ozone was found to be more effective for the improvement of BOD by breaking complex compounds, and colour removal of secondary effluent, it would likely be most useful if applied at an intermediate stage, after a partial biological treatment of mill effluent for the removal of simple organics. An ozone dose of 100 mg/L seemed to be most optimum for this particular case.

Having an understanding of ozonation for the removal of basic contaminants in pulp mill effluents, further research should be directed towards more specific problems such as the effects on organic halides and other complex compounds. Ultrafiltration technique would be helpful for finding the extent of degradation of the compounds in the pulp mill effluents.

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APPENDIX I

CHARACTERIZATION OF MILL EFFLUENTS

Table I.1 Biochemical Oxygen Demand (sample-1)

Sample	Unfiltered		Filtered		Respirometer
	15 mL sample/L	30 mL sample/L	15 mL sample/L	30 mL sample/L	BOD
Bleach	195	98	114	38	34
Effluent	195	126	109	43	
Primary	147	58	Depletion of oxygen by seed		65
Effluent	143	59			
			was more than the sample		
Secondary	67	54			34
Effluent	69	49			
Acid	151	36	59	60	
sewer	116	35	56	52	

Table I.2 Chemical Oxygen Demand (sample-1)

Sample	Unfiltered (mg/L)	Filtered (mg/L)
Acid Sewer	540	425
	564	646
Bleach Effluent	1553	1446
	1541	1494
	1569	32
		over titrated
Primary Effluent	608	443
	610	481
	622	501
Secondary Effluent	485	356
	505	358
	628	394

Table I.3 Total Organic Carbon (sample-1)

Sample	Unfiltered (mg/L)	Filtered (mg/L)
Acid Sewer	178	169
	180	171
	181	171
Bleach Effluent	852	745
	853	751
	855	772
Primary Effluent	169	153
	171	154
	172	154
Secondary Effluent	152	117
	167	118
	173	118

Table I.4 COD Test with Standard Solution of Potassium Hydrogen Phthalate

1. 500 mg Cl/L was added in the form of NaCl
2. $AgSO_4/H_2SO_4$ = 30 ml
3. $HgSO_4$ ~ 0.4 to 0.5 g

4. Amount of ferrous ammonium sulfate consumed for blank:
   1. 9.11 ml
   2. 9.14 "
   3. 9.45 "
   4. 9.48 "
   5. 9.52 "

Average= 9.34
Sandard deviation(Sd) = 0.2 ml

Actual COD (mg/L)	Estimated COD (mg/L)	Actual COD (mg/L)	Estimated COD (mg/L)
250	247	500	477
250	270	500	491
250	288	500	491
250	288	500	496
250	288	500	509
250	305	500	577

250 mg/L COD standard

Average = 281 mg/L
Standard deviation = 19.7 mg/L
Co-efficient of variation = Sd/Av. * 100 = 7 %

500 mg/L COD standard

Average = 507 mg/L
Standard deviation = 35.9 mg/L
Co-efficient of variation = Sd/Av. * 100 = 7%

Table I.5 Testing of Respirometer

1. Temperature was raised from 20 C to 20.3 C
2. Equalibrium time = 40 minutes

Flask No.	Micrometer reading (Initial)	Micrometer reading (Before) (Before correction) Test-1	Micrometer reading (After correction) Test-2
1	100	97.6	100.0
2	100	112.0	105.0
3	100	Check seal	100.0
4	100	101.0	100.0
5	100	98.6	100.0
6	100	96.6	100.0
7	100	98.8	98.4
8	100	97.8	100.0
9	100	98.0	100.0
10	100	99.0	100.0
11	100	98.2	96.6
12	100	99.0	100.0
13	100	99.0	100.0
14	100	145.4	100.0
15	100	99.0	96.0
16	100	Check seal	96.0
17	100	101.0	97.6
18	100	98.8	100.0
19	100	102.0	100.0
20	100	98.6	100.0

Table I.6 Optimization of Dilution for Bleach Effluent

Dilution	BOD5(mg/L)	BOD10 (mg/L)	BOD20(mg/L)
Respirometer	58	131	181
Bottle-method			
30 mL sample/1500	99	-	432
20 mL sample/1500	150	314	466
15 mL sample/1500	201	309	459
10 mL sample/1500	210	287	483
5 mL sample/1500	202	334	412

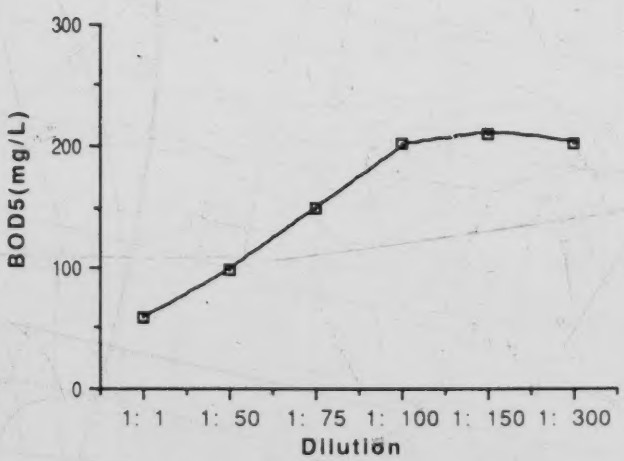

Figure I.1 Dilution Optimization for Bleach Effluent

Table I.7 Optimization of Dilution for Primary Effluent

Dilution	BOD5(mg/L)	BOD10 (mg/L)	BOD20(mg/L)
Respirometer (av)	140	193	249
Bottle-method			
30 mL sample/1500	189	-	278
20 mL sample/1500	181	182	286
15 mL sample/1500	150	221	269
10 mL sample/1500	190	239	319
5 mL sample/1500	316	412	424

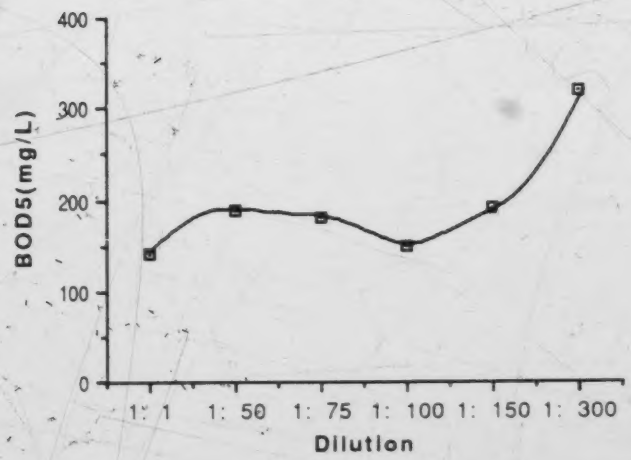

Figure I.2 Dilution Optimization for Primary Effluent

Table I.8 Optimization of Dilution for Secondary Effluent

Dilution	BOD5(mg/L)	BOD10 (mg/L)	BOD20(mg/L)
Respirometer	22	65	98
Bottle-method			
60 mL sample/1500	37	-	99
40 mL sample/1500	45	79	121
30 mL sample/1500	43	84	118 135
20 mL sample/1500	-	-	191 148
10 mL sample/1500			148 257

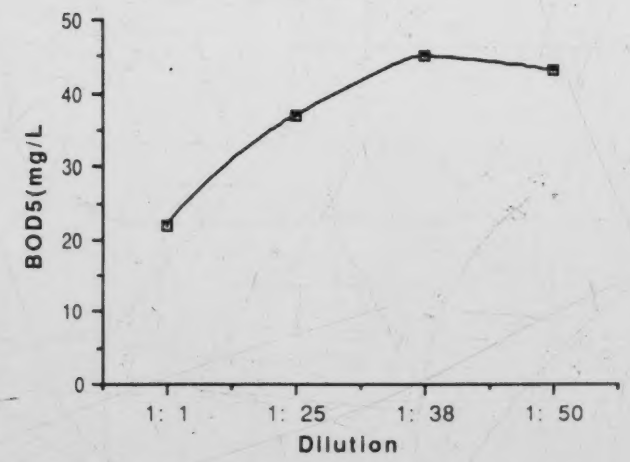

Figure I.3 Dilution Optimization for Secondary Effluent

Table I.9 Ke and Lo for Mill Effluents

Sample	K(e)/day	Lo (mg/L)
Bleach effluent		
Respirometer	0.06	302
range	0.04 to 0.08	227 to 378
Bottle-method	0.08	599
range	0.04 to 0.11	448 to 750
Primary effluent		
Respirometer	0.35	198
range	0.30 to 0.39	192 to 204
	0.19	267
	0.16 to 0.22	252 to 282
Bottle-method	0.18	293
range	0.10 to 0.27	246 to 339
Secondary effluent		
Respirometer	0.04	181
range	0.03 to 0.05	151 to 211
Bottle-method	0.05	200
range	0.03 to 0.07	150 to 250

Table I.10 Chemical Oxygen Demand and Total Organic Carbon

1. $HgSO_4$ ~ 1 g
2. $AgSO_4/H_2SO_4$ = 30 mL

Sample	COD (mg/L) Unfiltered	COD (mg/L) Filtered	TOC (mg/L) Unfiltered	TOC (mg/L) Filtered	COD/TOC
Bleach	2787	2627	860	863	Unfiltered
effluent	2793	2695	861	864	3.24
	2810	2764	862	865	Filtered
median	2793	2695	861	864	3.11
Primary	782	669	269	236	Unfiltered
effluent	786	712	269	237	3.00
	800	772	270	237	Filtered
median	786	712	269	237	2.92
Secondary	519	395	160	126	Unfiltered
effluent	569	398	160	127	3.56
	574	422	161	128	Filtered
median	569	398	160	127	2.92

For industrial wastes the COD/TOC ratio ~ 3 to 4

Table I.11 Suspended Solids for Mill Effluents

Sample	Total Suspended Solids (mg/L) 105 C	Volatile Suspended Solids (mg/L) 550 C
Bleach effluent	76	58
	80	61
	83	65
Primary effluent	102	79
	116	80
	122	86
Secondary effluent	90	70
	96	78
	102	88

APPENDIX II

OZONATION OF BLEACH EFFLUENT

Table II.1 Biochemical Oxygen Demand (mg/L) for Bleach Effluent

Days	Raw sample	Oxygen	50-Ozone Run#1	50-Ozone Run#2	100-Ozone Run#1	100-Ozone Run#2
1	52	-	14	82	21	49
2	60	5	19	89	53	80
3	112	84	92	158	125	159
4	201	86	147	200	154	189
5	211	173	189	240	188	207
5	216	178	199	247	188	213
5	221	192	207	256	203	214
7	278	251	240	279	239	280
7	295	256	248	292	241	280
7	300	269	256	294	242	-
11	271	255	264	349	246	310
11	313	258	277	349	267	312
11	324	279	284	349	283	317
20	324	256	311	284	248	303
20	341	302	312	301	296	314
20	350	308	316	303	305	316
20	356	311	343	306	308	320
20	358	314	344	313	312	323
20	359	-	366	315	316	347

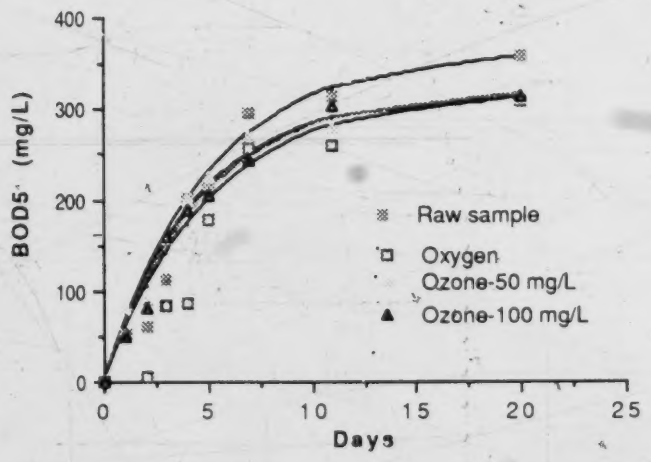

Figure II.1 Biochemical Oxygen Demand for Bleach Effluent

Table II.2 COD and TOC for Bleach Effluent

SAMPLE	COD (mg/L) (Unfiltered)	COD (mg/L) (Filtered)	TOC (mg/L) (Unfiltered)	TOC (mg/L) (Filtered)
Raw sample	1153	969	438	424
	1169	986	438	429
	1190	1017	438	429
Median	1169	986	438	429
Oxygen	1130	997	434	429
	1150	1003	436	431
	1170	1008	438	432
Median	1150	1003	436	431
50 mg O3/L	1073	965	424	430
Run#1	1093	997	427	431
	1117	1005	435	432
Median	1093	997	427	431
50 mg O3/L	1034	942	435	430
Run#2	1071	965	438	432
	1106	969	438	434
Median	1071	965	438	432
100 mg O3/L	1038	879	421	411
Run#1	1059	918	426	413
	1110	961	427	415
Median	1059	918	426	413
100 mg O3/L	1059	938	432	409
Run#2	1077	960	433	409
	1154	983	435	412
Median	1077	960	433	409

Table II.3 Suspended Solids for Bleach Effluent

SAMPLE	Total Suspended Solids (mg/L)	Volatile Suspended Solids (mg/L)
Raw sample	197	157
	200	180
	250	217
mean	217	185
Oxygen	183	150
	197	163
	207	170
mean	196	161
50 mg O3/L	157	127
Run#1	190	150
	200	163
mean	182	147
50 mg O3/L	237	193
Run#2	247	197
	250	200
mean	245	197
100 mg O3/L	200	147
Run#1	207	153
	207	160
mean	205	153
100 mg O3/L	190	157
Run#2	200	163
	223	180
mean	204	167

Table II.4 Colour Removal for Bleach Effluent

Sample	True colour (Pt/Co units)	Colour removal (Pt/Co units)	% Removal
Raw sample	2430	-	
Oxygen	2430	-	
50 mg O3/L (Run#1)	1750	680	28
50 mg O3/L (Run#2)	1685	745	31
100 mg O3/L (Run#1)	1135	1295	53
100 mg O3/ (Run#2)	1070	1360	56

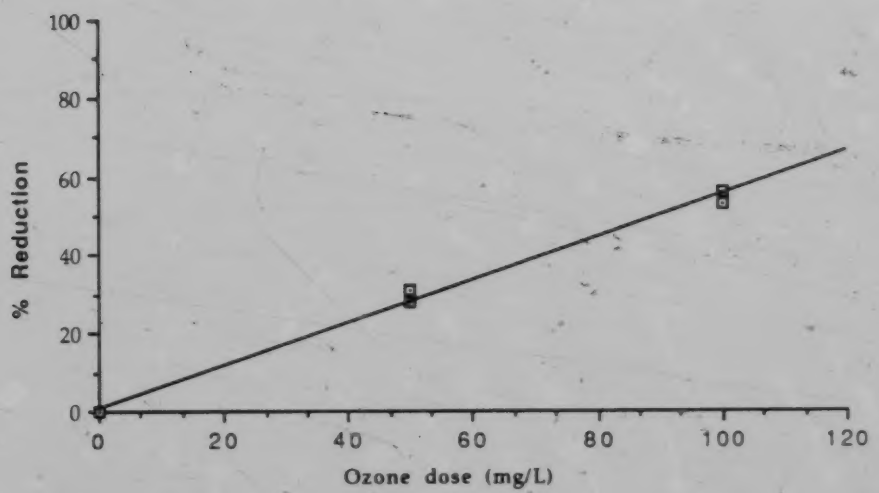

Figure II.5 % Colour Removal for Bleach Effluent

APPENDIX III

OZONATION OF PRIMARY EFFLUENT

Table III.1 Biochemical Oxygen Demand (mg/L) for Primary Effluent

Days	Raw sample	Oxygen	50-Ozone Run#1	50-Ozone Run#2	100-Ozone Run#1	100-Ozone Run#2
2	136	117	110	113	118	87
3	166	143	162	155	160	166
4	200	137	180	182	177	160
5	186	171	176	158	154	159
5	205	174	179	170	178	182
5	230	183	193	177	179	182
6	202	181	194	178	188	185
7	196	178	174	174	207	199
7	204	190	208	194	218	203
7	211	203	210	202	219	208
10	214	203	210	210	222	208
10	228	208	211	210	222	209
10	238	211	221	223	236	218
20	267	299	268	238	265	247
20	279	308	285	252	267	267
20	279	314	286	257	290	274

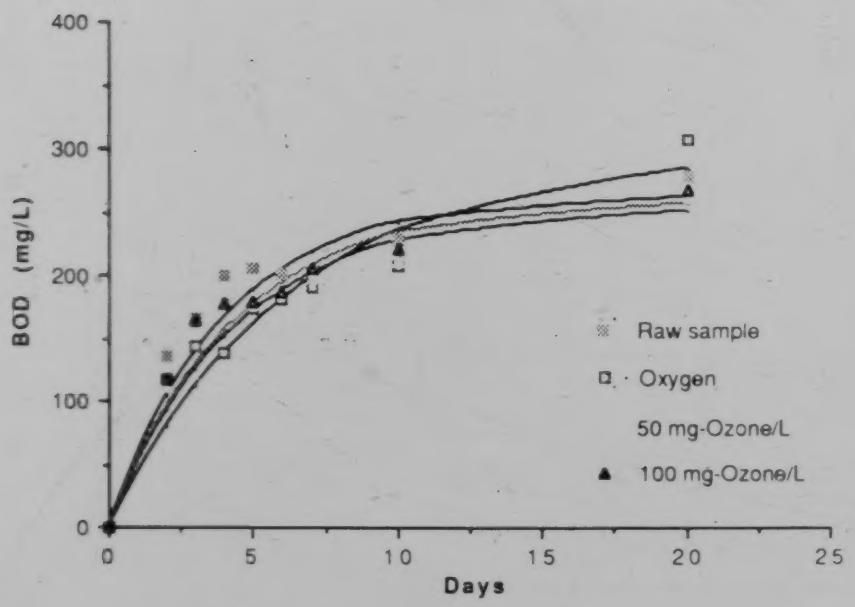

Figure III.1 Biochemical Oxygen Demand for Primary Effluent

Table III.2 COD and TOC for Primary Effluent

SAMPLE	COD (mg/L) (Unfiltered)	COD (mg/L) (Filtered)	TOC (mg/L) (Unfiltered)	TOC (mg/L) (Filtered)
Raw sample	688	633	243	218
	694	651	243	218
	696	788	244	219
Oxygen	690	521	234	205
	698	621	236	211
	706	625	236	212
50 mg O3/L	676	555	236	216
Run#1	678	588	237	218
	688	594	238	218
50 mg O3/L	651	566	236	220
Run#2	719	589	238	222
	725	611	240	222
100 mg O3/L	592	566	225	216
Run#1	621	574	226	217
	643	588	226	218
100 mg O3/L	657	523	230	216
Run#2	662	608	231	218
	694	613	232	219

Table III.3 Total and Volatile Suspended Solids for Primary Effluent

SAMPLE	TOTAL SUSPENDED SOLIDS (mg/L)	VOLATILE SUSPENDED SOLIDS (mg/L)
Raw sample	83	47
	83	50
	87	57
mean	84	51
Oxygen	63	37
	70	43
	77	67
mean	70	49
50 mg O3/L	70	50
Run#1	80	53
	63	50
mean	71	51
50 mg O3/L	63	37
Run#2	70	53
	80	40
mean	72	43
100 mg O3/L	63	50
Run#1	67	50
	60	43
mean	63	48
100 mg O3/L	73	50
Run#2	70	47
	40	23
mean	61	40

Table III.4 Colour Standard Data for Primary Effluent

Standard Colour (Pt/Co units)	Absorbance	Transmittance
0	0	100
25	0.003	99.0
50	0.015	96.4
100	0.029	93.3
150	0.046	90.1
200	0.061	86.9
250	0.073	84.2

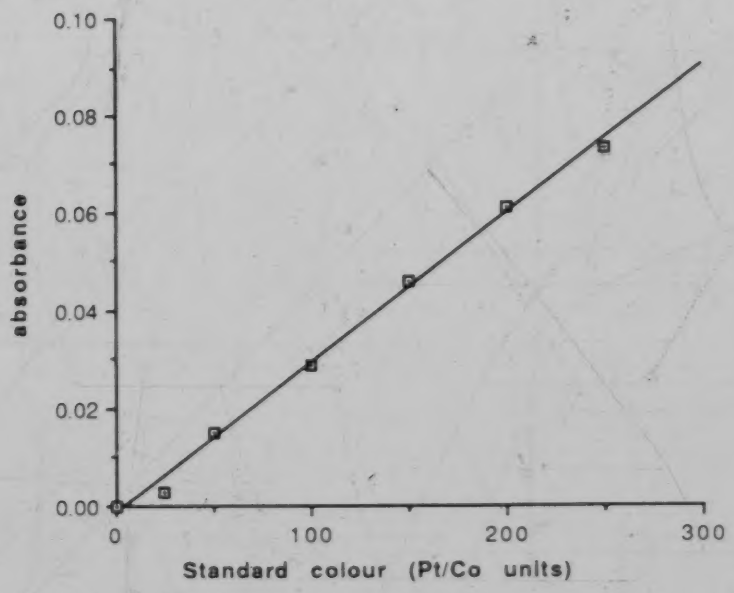

Figure III.4 Colour Standard Graph for Primary Effluent

Table III.5 Colour Removal for Primary Effluent

Sample	True Colour (Pt/Co units)	Colour Removal (Pt/Co units)	% Removal
Raw sample	1850	-	
Oxygen	1750	-	
50 mg O3/L (Run#1)	1010	840	45
50 gm O3/L (Run#2)	990	860	47
100 mg O3/L (Run#1)	525	1325	72
100 mg O3/L (Run#2)	490	1360	74

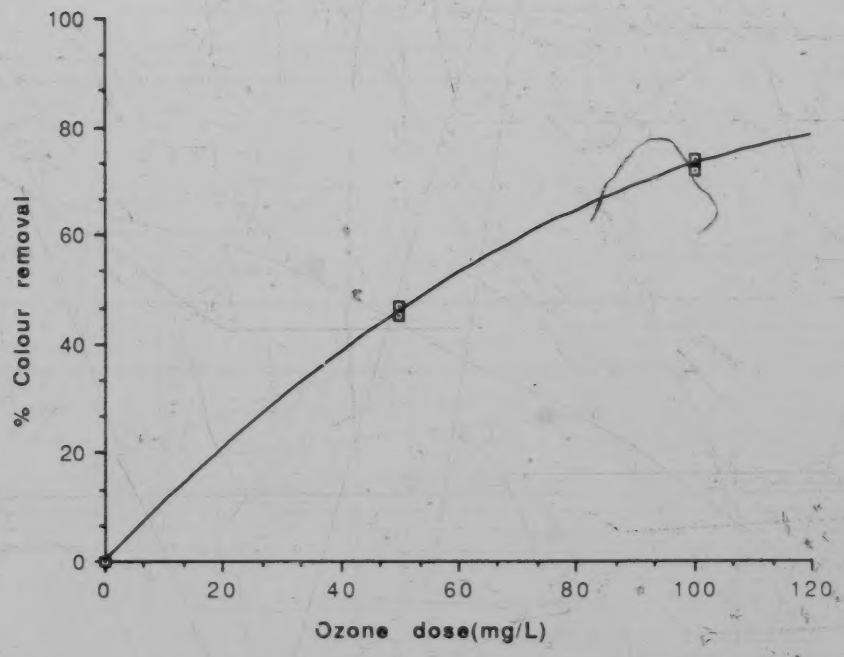

Figure III.6 % Colour Removal for Primary Effluent

APPENDIX IV

OZONATION OF SECONDARY EFFLUENT
(Run#1 and Run#2)

Table IV.1 Biochemical Oxygen Demand (mg/L) for Secondary Effluent

Days	Raw Sample	Oxgen	50-Ozone Run#1	50-Ozone Run#2	100-Ozone Run#1	100-Ozone Run#2
2	35	38	34	37	50	50
3	21	37	39	51	52	82
4	35	40	64	53	59	57
5	26	33	42	37	59	66
5	26	37	53	62	67	67
5	46	55	59	62	69	74
6	33	53	57	58	75	78
7	34	34	56	32	74	82
7	38	54	57	43	75	86
7	50	59	72	44	92	86
10	52	46	58	58	70	78
10	56	50	60	60	70	89
10	59	60	66	66	86	99
20	52	58	67	85	85	102
20	56	62	78	107	86	115
20	66	78	90	117	106	116

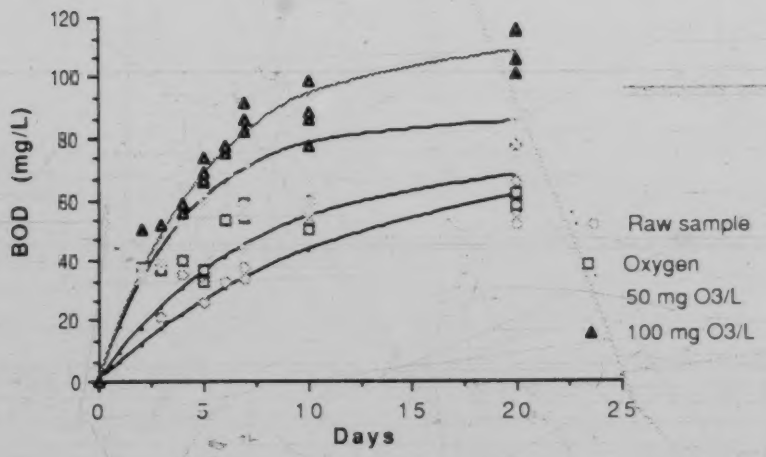

Figure IV.1 Biochemical Oxygen Demand for Secondary Effluent

Table IV.2 COD and TOC for Secondary Effluent

SAMPLE	C.O.D. (Unfiltered)	C.O.D. (Filtered)	T.O.C. (Unfiltered)	T.O.C. (Filtered)
Raw sample	402	336	149	136
	448	367	154	136
	653	379	154	138
Oxygen	441	336	148	130
	453	336	149	131
-	464	-	149	131
50mg/l Ozone	383	296	147	125
Run#1	454	301	147	125
	456	311	147	127
50mg/l Ozone	384	282	147	126
Run#2	410	313	148	127
	415	343	149	127
100gm/lOzone	412	211	142	124
Run#1	415	340	142	125
-	-	-	143	126
100gm/lOzone	342	290	144	127
Run#2	363	292	145	128
	394	301	-	128

Table IV.3 Total and Volatile Suspended Solids for Secondary Effluent

SAMPLE	Total Suspended Solids (mg/L)	Volatile Suspended Solids (mg/L)
Raw sample	73	67
	83	63
	93	67
mean	83	66
Oxygen	77	63
	70	60
	63	53
mean	70	59
50-Ozone	77	63
Run#1	80	67
	83	67
mean	80	66
50-Ozone	77	63
Run#2	70	63
	73	63
mean	73	63
100-Ozone	63	60
Run#1	57	43
	70	60
mean	63	54
100-Ozone	73	60
Run#2	40	30
	60	57
mean	58	49

Table IV.4 Colour Standard for Secondary Effluent

Standard colour (Pt/Co units)	Absorbance	Transmittance
0	0.000	100
25	0.006	98.1
50	0.015	96.1
100	0.031	93.0
150	0.047	89.9
200	0.060	87.0
250	0.076	83.9
500	0.154	70.0

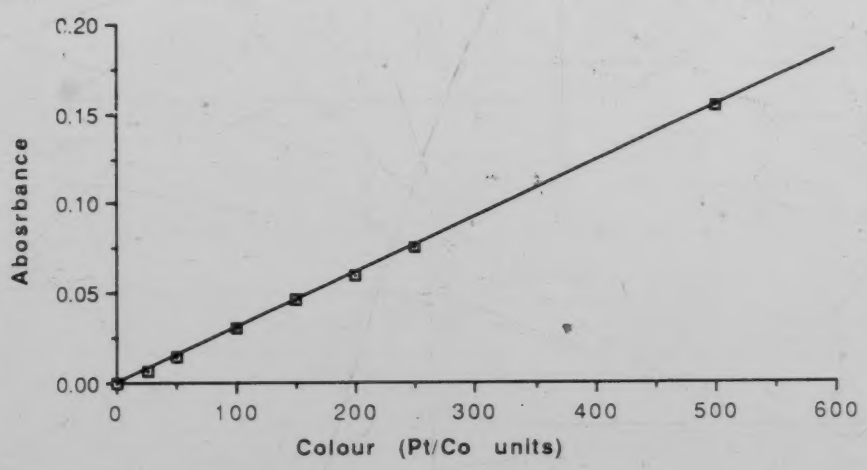

Figure IV.4 Colour Standard Graph for Secondary Effluent

Table IV.5 Colour Removal for Secondary Effluent

Sample	True colour (Pt/Co units)	Colour removal (Pt/Co units)	% Reduction
Raw sample	1525	-	0
Oxygen	1550	-	0
50 mg O3/L (Run#1)	575	950	62
50 mg O3/L (Run#2)	500	1025	67
100 mg O3/L (Run#1)	300	1225	80
100 mg O3/L (Run#2)	250	1275	84

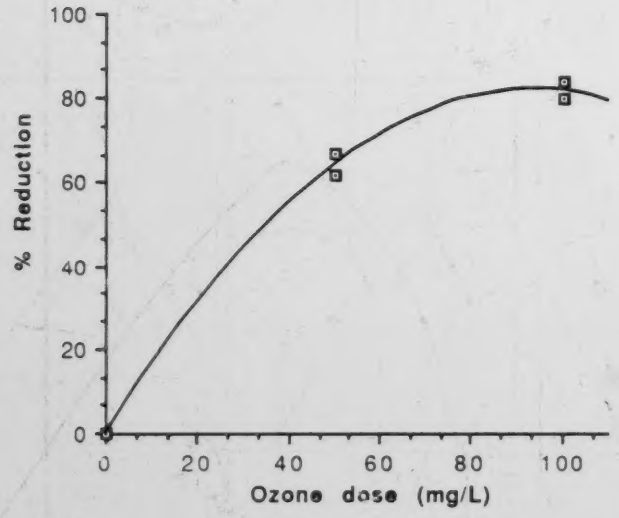

Figure IV.6 % Colour Reduction for Secondary Effluent

APPENDIX V

OZONATION OF SECONDARY EFFLUENT
(Run3# and Run#4)

Table V.1 Biochemical Oxygen Demand (mg/L) for Secondary Effluent

Days	Raw sample	Oxygen	50-Ozone Run#3	50-Ozone Run#4	100-Ozone Run#3	100-Ozone Run#4
3	18	31	47	43	50	51
4	32	24	35	43	49	54
5	31	31	40	43	40	42
5	32	37	50	45	48	58
5	57	39	54	69	50	64
6	32	18	23	46	65	68
7	37	31	46	58	58	74
7	38	35	52	59	75	82
7	43	37	68	66	78	87
10	45	42	55	54	85	71
10	59	42	63	56	87	72
10	59	42	71	58	91	77
17	54	55	81	86	110	109
20	62	61	71	78	86	110
20	71	67	75	85	96	112
20	79	72	81	85	105	115

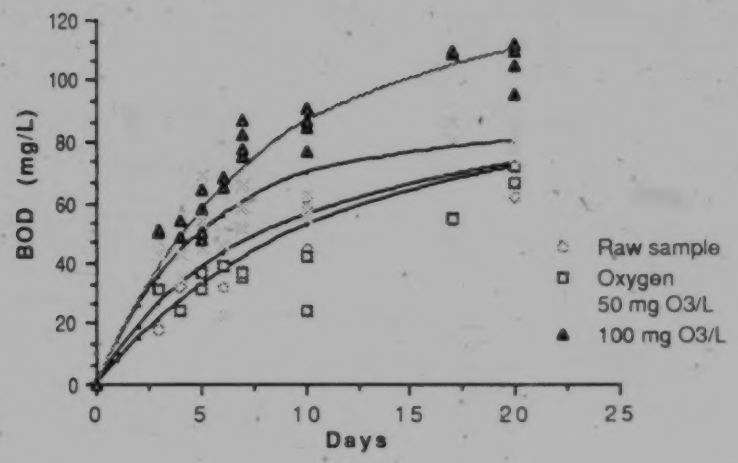

Figure V.1 Biochemical Oxygen Demand for Secondary Effluent

Table V.2 COD and TOC for Secondary Effluent

SAMPLE	COD (mg/L) (Unfiltered)	COD (mg/L) (Filtered)	TOC (mg/L) (Unfiltered)	TOC (mg/L) (Filtered)
Raw sample	512	478	197	148
	530	592	200	149
	566	636	204	149
Oxygen	-	-	195	144
	566	444	196	146
	570	602	216	148
50 mg O3/L	520	-	187	132
Run#1	520	434	190	133
	536	458	218	133
50 mg O3/L	-	-	188	134
Run#2	520	426	198	135
	588	488	211	136
100 mg O3/L	488	454	184	132
Run#1	498	490	185	135
	520	506	190	138
100 mg O3/L	520	-	183	133
Run#2	530	378	188	134
	536	424	190	136

Table V.3 Total and Volatile Suspended Solids for Secondary Effluent

SAMPLE	Total Suspended Solids (mg/L)	Volatile Suspended Solids (mg/L)
Raw sample	103	77
	110	80
	110	87
mean	108	81
Oxygen	97	73
	103	83
	110	87
mean	103	81
50 mg O3/L	97	77
Run#1	100	80
	100	83
mean	99	80
50 mg O3/L	93	70
Run#2	97	70
	100	77
mean	97	72
100 mg O3/L	83	60
Run#1	93	70
	93	77
mean	90	69
100 mg O3/L	103	67
Run#2	103	70
	110	80
mean	105	72

Table V.4 Colour Standard for Secondary Effluent

Standard colour (Pt/Co units)	Absorbance	Transmittance
0	0	100
25	0.010	97.2
50	0.018	95.8
100	0.035	92.0
150	0.052	89.0
200	0.064	86.5
250	0.080	83.0
500	0.162	69.0

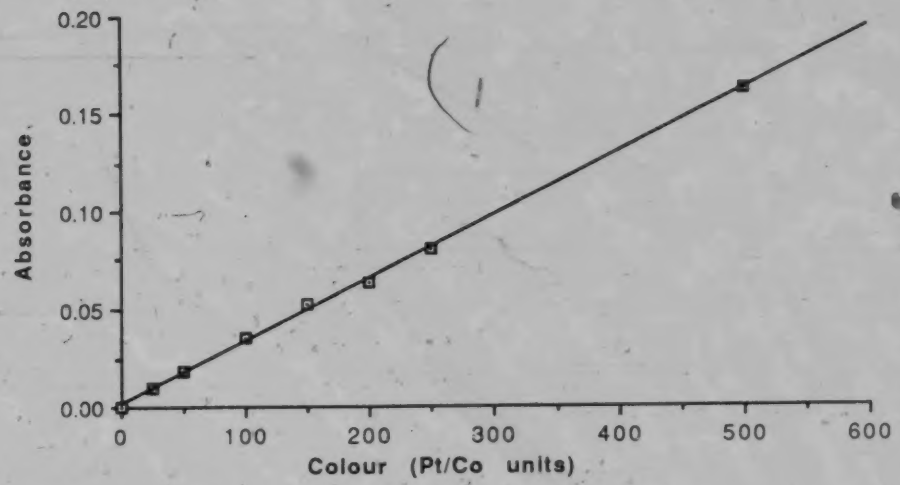

Figure V.4 Colour Standard Plot for Secondary Effluent

Table V.5 Colour Removal for Secondary Effluent

SAMPLE	True colour (Pt/Co units)	Colour reduction (Pt/Co units)	% Reduction
Raw sample	1720	-	-
Oxygen	1750	-	-
50 mg O3/L Run#1	625	1095	64
50 mg O3/L Run#2	625	1095	64
100 mg O3/L	250	1470	86
Run#1	270	1450	84
100 mg O3/L	280	1440	84
Run#2	270	1450	84

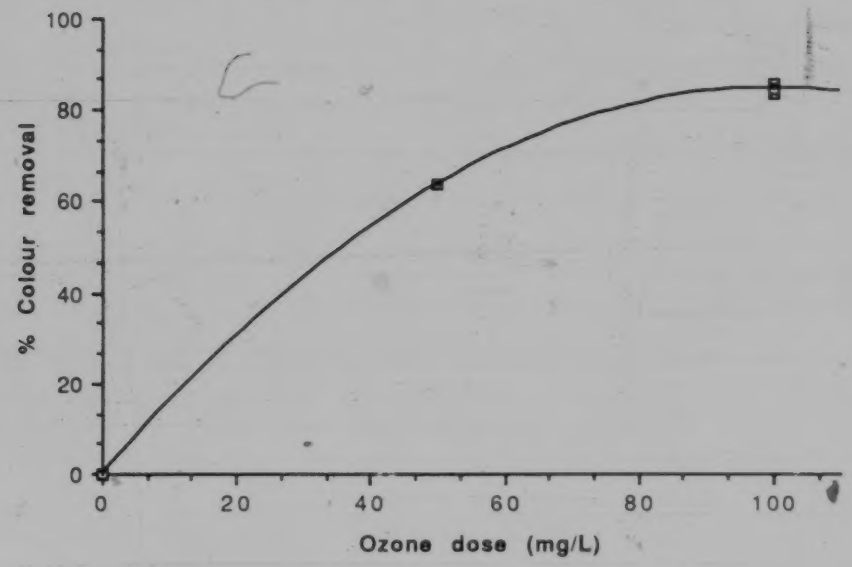

Figure V.6 % Colour Removal for Secondary Effluent

APPENDIX VI

OZONATION OF SECONDARY EFFLUENT
(Run #5)

Table VI.1 Biochemical Oxygen Demand (mg/L) for Secondary Effluent

Days	Raw sample	Oxygen	50 mg O3/L	100 mg O3/L	150 mg O3/L
5	33	31	40	51	61
5	36	34	46	63	63
5	55	43	48	69	73
10	63	65	60	92	97
10	65	67	67	103	98
10	70	67	72	105	108
20	90	89	88	112	110
20	92	91	89	115	123
20	102	91	100	127	126

Table VI.2 COD and TOC for Secondary Effluent

SAMPLE	COD (mg/L) (Unfiltered)	COD (mg/L) (Filtered)	TOC (mg/L) Unfiltered)	TOC (mg/L) (Filtered)
Raw sample	462	381	205	160
	524	406	207	161
	599	408	209	162
Oxygen	461	265	209	150
	492	373	209	152
	502	402	213	152
50 mg O3/L	439	325	197	139
	446	363	199	140
	473	390	201	140
100 mg O3/L	439	307	195	144
	451	360	199	145
	483	361	201	146
150 mg O3/L	99	286	190	139
	385	296	191	139
	420	361	192	140

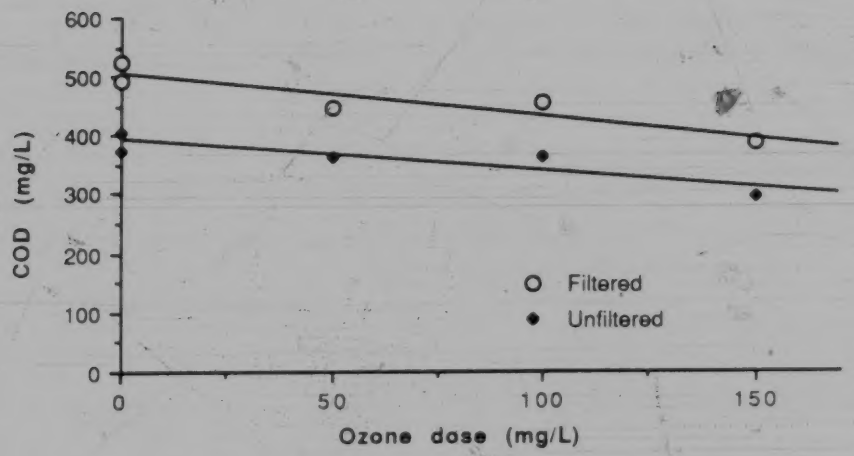

Figure VI.1 Chemical Oxygen Demand for Secondary Effluent

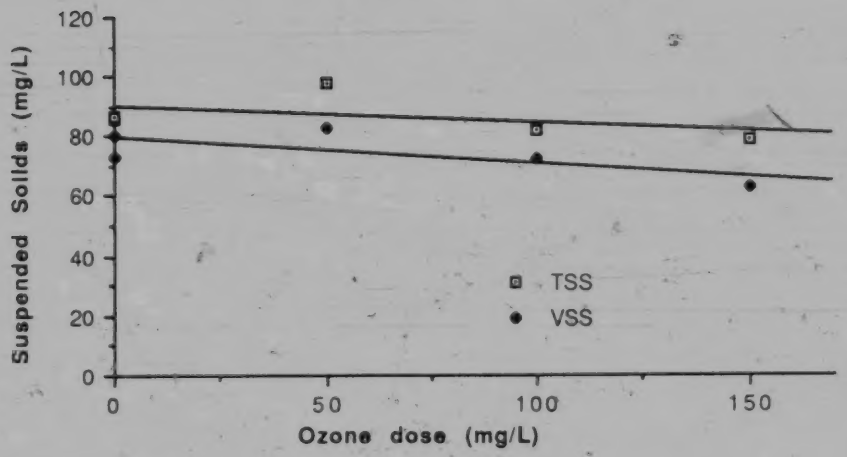

Table VI.2 Total and Volatile Suspended Solids for Secondary Effluent

Table VI.3 Total and Volatile Suspended Solids for Secondary Effluent

Sample	Total Suspended Solids (mg/L)	Volatile Suspended Solids (mg/L)
Raw sample	83	70
	85	70
	90	80
mean	86	73
Oxygen	87	77
	87	80
	88	83
mean	87	80
50 mg O3/L	93	83
	98	83
	103	83
mean	98	83
100 mg O3/L	80	60
	83	77
	83	83
mean	82	72
150 mg O3/L	77	60
	77	63
	83	67
mean	79	63

Table VI.4 Colour Standard for Secondary Effluent

Standard Colour (Pt/Co units)	Absorbance	Transmittance
0	0	100
50	0.020	95.5
100	0.035	92
150	0.045	90
200	0.066	85.8
250	0.078	83
250	0.080	83
500	0.165	68.5

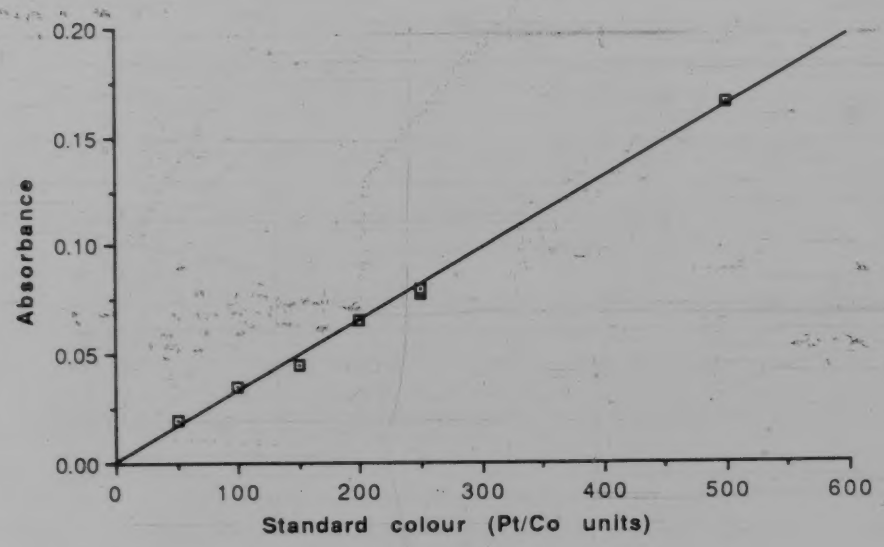

Figure VI.3 Colour Standard Plot for Secondary Effluent

Table VI.5 Colour Reduction for Secondary Effluent

Sample	True colour (Pt/Co units)	Colour reduction (Pt/Co units)	% Reduction
Raw sample	1575	-	-
Oxygen	1575	-	-
50 mg O3/L	660	915	58
100 mg O3/L	370	1205	77
150 mg O3/L	215	1360	86

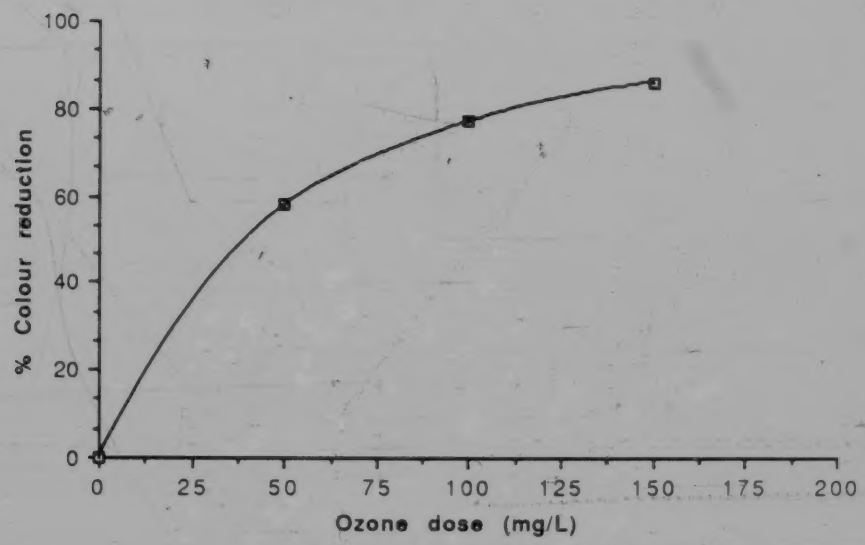

Figure VI.5 % Colour Reduction for Secondary Effluent

APPENDIX VII

OZONATION OF SECONDARY EFFLUENT
(Run #6)

Table VII.1 Biochemical Oxygen Demand (mg/L) for Secondary Effluent

Days	Raw sample	Oxygen	50-Ozone	100-Ozone	150-Ozone	200-Ozone
5	41	39	55	58	63	58
5	38	43	56	71	63	90
5	52	46	58	72	81	98
10	66	70	90	95	95	109
10	66	74	90	99	95	118
10	70	75	92	101	100	121
20	100	103	124	157	150	141
20	108	116	130	158	150	144
20	123	124	132	159	151	155

Table VII.2 COD and TOC for Secondary Effluent

SAMPLE	COD (mg/L) (Unfiltered)	COD (mg/L) (Filtered)	TOC (mg/L) (Unfiltered)	TOC (mg/L) (Filtered)
Raw sample	398	359	197	144
	451	367	199	145
	473	676	201	145
Oxygen	391	352	198	142
	441	372	198	143
	703	392	199	143
50 mg O3/L	430	342	187	135
	441	347	187	136
	465	352	189	136
100 mg O3/L	398	309	178	130
	437	338	178	131
	445	373	184	131
150 mg O3/L	383	297	167	128
	391	309	168	128
	391	338	171	129
200 mg O3/L	348	305	163	126
	387	309	163	127
	447	312	167	127

Table VII.3 Total and Volatile Suspended Solids for Secondary Effluent

SAMPLE	Total Suspended Solids (mg/L)	Volatile Suspended Solids (mg/L)
Raw sample	90	70
	93	70
	97	73
mean	93	71
Oxygen	87	70
	90	73
	97	77
mean	91	73
50 mg O3/L	90	67
	93	77
	97	77
mean	93	73
100 mg O3/L	87	67
	90	73
	90	77
mean	89	72
150 mg O3/L	77	63
	80	63
	80	67
mean	79	64
200 mg O3/L	77	63
	80	63
	87	63
mean	81	63

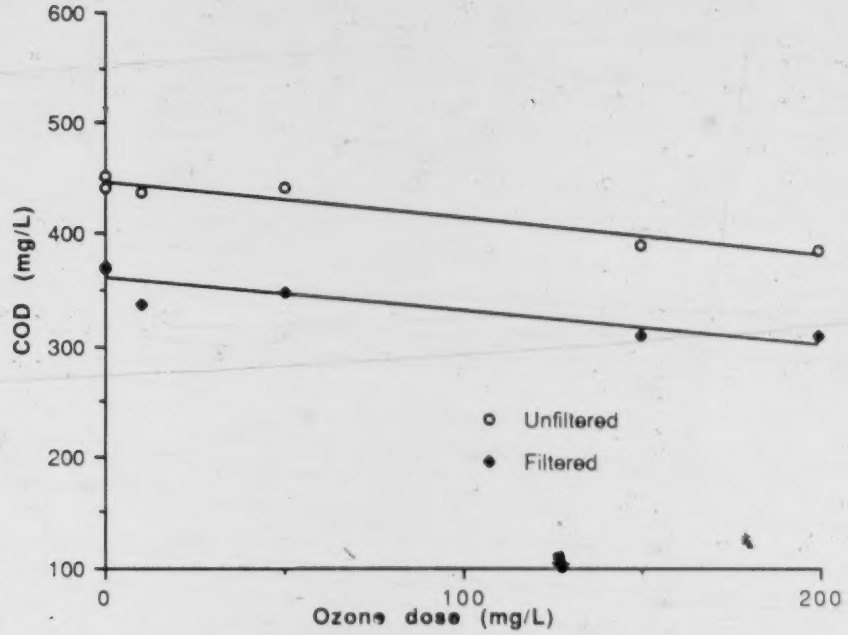

Figure VII.1 Chemical Oxygen Demand for Secondary Effluent

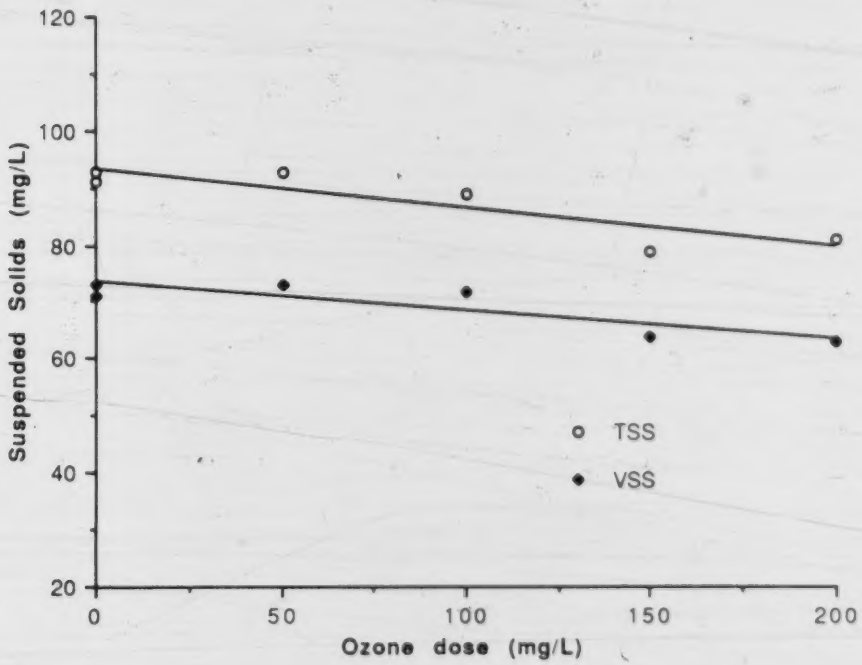

Figure VII.2 Total and Volatile Suspended Solids for Secondary Effluent

Table VII.4 Colour Standard Data for Secondary Effluent

Standard Colour (Pt/Co units)	Absorbance Run#1	Transmittance Run#1	Absorbance Run#2	Transmittance Run#2
0	0	100	0	100
25	0.015	96.0	0.015	96.0
50	0.021	94.0	0.022	95.0
100	0.036	92.0	0.035	92.0
150	0.052	89.0	0.052	92.0
200	0.069	85.5	0.068	85.5
250	0.081	83.0	0.085	82.0
500	0.162	69.0	0.170	69.0
500	0.162	69.0	0.168	68.0

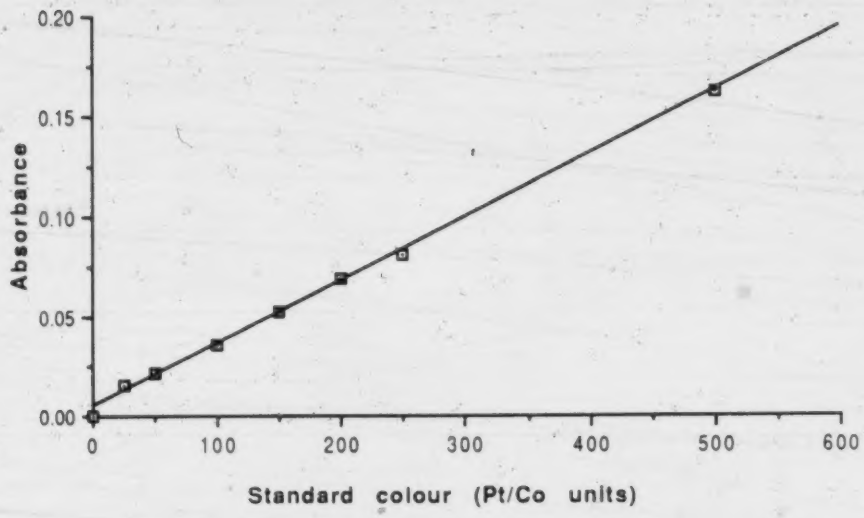

Figure VII.3 Colour Standard Plot for Secondary Effluent

Table VII.5 Colour Reduction for Secondary Effluent

Sample	True colour (Pt/Co units)	Colour reduction (Pt/Co units)	% Reduction
Raw sample	1770		
Oxygen	1820		
50 mg O3/L	710	1060	60
100 mg O3/L	320	1470	82.5
150 mg O3/L	170	1600	89.8
200 mg O3/L	185	1585	89.4

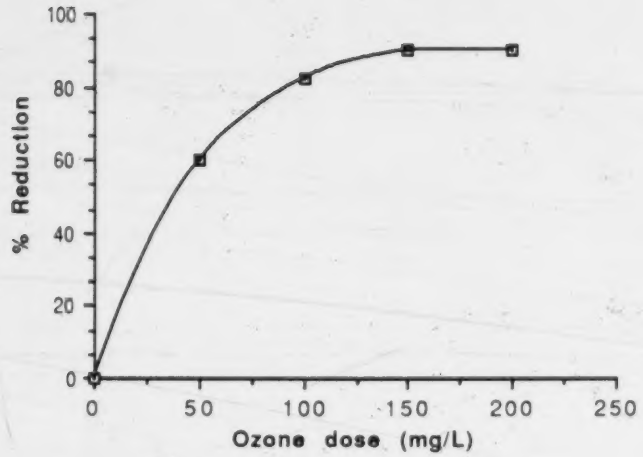

Figure VII.5 Colour Reduction for Secondary Effluent

APPENDIX VIII

CALIBRATION OF OZONE SYSTEM

VIII.1 Calibration of Ozone Generation System

VIII.1.1 Oxygen Flow Rate Measurement Using Wet Test Meter

With top of the rotameter float touching "10" mark
flow rate = 3L in 77 seconds
= 2.338 L/min
Corrected Gas Flow Rate = $(P_m)(T_s) / (P_s)(T_m) * V_m$
Room temperature = 20° C
Barometric pressure = 700 mm Hg
P_m = (Barometric pressure + Gauge pressure - P_w)
= (700 - 17.535)
= 682 mm Hg
V_s = 682 * 273 * 2.338/ 760 * 293
= 1.96 L/min

VIII.1.2 Measurement of Reactor Volume

1. Volume of the reactor measured by adding water
V = (475 + 5 +2.5)
= 482.5 mL

2. Volume of the reactor measured by weight/density method:
Temperature of the water = 19° C
Density of water at 19° C = 0.99843 g/mL
Weight of the beaker + water = 788.90 g
Weight of the beaker = 312.86 g
Weight of the water = 476.04 g
Volume of the water=weight (g)/ density(g/mL)
=476.04 / 0.99843
= 476.8 mL
Error = (482.5 - 476.8) *100 / 476.8 = 1.19%

VIII.1.3 Volume of the Spherical Section of the Reactor

1. Measured by adding water = (500 + 500 + 150 +33)=1083 mL

2. Measured by weight / density method:
   Weight of the beaker + water = 1379.7 g
   Weight of the beaker = 309.7 g
   Weight of the water = 1070 g
   Volume of the water = 1070 / 0.99843 = 1071.7 mL
   Error = (1083 - 1071.7) * 100 / 1071.7 = 1.05%

VIII.1.4 Amount of Ozone Diffused into Cylindrical Part of the Reactor

VIII.1.4.1 minutes ozone and 10 minutes nitrogen @ 3 L/min

Molarity of thiosulfate = 0.005 M
1 mL of 0.005 M thiosulfate = 120 μg O_3 (Standard Methods, APHA, AWWA, WPCF, 1985)
Volume of thiosulfate consumed for titration = 9.06 ml
Amount of ozone diffused into the reactor =9.06 * 0.12
= 1.1 mg O_3

VIII.1.4.2 10 minutes ozone and 20 minutes nitrogen @ 3 L/min

Volume of thiosulfate consumed = 4.2 mL
Amount of ozone diffused = 4.2 * 0.12 = 0.5 mg O_3

VIII.1.5 % Concentration of Ozone/Oxygen Mixture Required for Ozone Doses

Volume of the sample in the reactor = 477 mL

For 50 mg O_3/L dose, amount of ozone required = 50 * 477 / 1000
= 23.8 mg O_3

For 100 mg O_3/L dose, amount of ozone required = 47.7 mg O_3

For 150 " " " " " " " " " " " = 71.5 mg O_3

For 200 " " " " " " = 95.3 mg O_3

Volume of the spherical section of the reactor = 1083 ml

Density of the Ozone / Oxygen mixture = $1.3285 * 10^{-3}$ g / mL

Mass of the gas mixture = 1083 mL* 1.3285 *10^{-3} mg /mL
= 1438.8 mg

% Ozone Concentration
= mass of ozone required * 100/ mass of gas

For 50 mg O_3 /L dose = 23.8 * 100 /1438.8
= 1.654 % (wt / wt)

For 100 mg O_3 /L dose = 47.7 * 100 / 1438.8
= 3.314 % (wt / wt)

For 150 mg O_3 /L dose = 71.5 * 100 / 1438.8
= 4.969 % (wt / wt)

For 200 mg O_3 /L dose = 95.3 * 100 / 1438.8
= 6.623 % (wt / wt)

APPENDIX IX

STATISTICAL CALCULATIONS

IX.1 Statistical test for 5-day BOD Improvements

Raw sample	Oxygen	50 mgO_3/L	100 mgO_3/L
26	37	53	67
		59	67
32	37	50	50
		45	58
36	34	46	63
41	39	56	71
X" = 33.75	36.75	51.50	62.70
n = 4	4	6	6
S_2 = 40.25	4.25	30.70	57.90
F(test) S_2 / S_1			
	0.105	0.763	1.438
F(3,3)0.05 = 9.28		F(5,3)0.05 = 9.01	

Since the tabulated value is greater than calculated, the data can be pooled together.

Oxygen	50 mgO_3/L	100 mgO_3/L
(d)	(d)	(d)
11	27	41
	33	41
5	18	8
	13	26
0	10	27
2	15	30
---	---	---
d" = 4.5	19.3	30.5
n = 4	6	6
S_2 = 16.25	78.7	81.9
S = 4.03	8.87	9.04
S_d = 2.015	3.621	3.690
t (calculated) = 2.233	5.331	8.265
t (3, 0.025) = 3.182	t (5,0.025) = 2.571	
(table values)	t (5,0.001) = 5.893	

Since the calculated values for "t" are higher than table values, therefore the Ho(null hypothesis) is incorrect and there is a significant improvement in BOD_5 of the secondary effluent with ozonation.

IX.2 't' test for Total Suspended Solids (mg/L)

Raw sample	Oxygen	50 mg O3/L	100 mg O3/L
83	70	80	63
108	103	73	58
86	87	99	90
93	91	97	105
		98	82
		93	89
X" = 92.50	87.75	98.00	81.17
n = 4	4	6	6
$S_1^2 = 124.3$	$S^2_2 = 186.3$	$S^2_3 = 197.3$	$S^2_4 = 524.9$
F(test)	S12 / S22		
	1.498	1.587	4.220

F(3,3) 95% = 9.280

Since the tabulated value is greater than calculated value, it means the variance is same, the data can be pooled together and treated as on paired basis.

$S_2 = \Sigma (d - d")2 / np - 1$

$S_d = S / \sqrt{np}$

$t = d" / S_d$

d = (Raw sample - Oxygen or 50 mgO_3/L or 100 mgO_3/L)

Oxygen (d)	50 mg O_3/L (d)	100 mg O_3/L (d)
13	3	20
5	10	25
0	9	18
2	11	3
	0	4
	0	4
$\bar{d}$" = 5.0	5.5	12.3
n = 4	6	6

For Oxygenated sample

$S_2 = 32.66$

$S = 5.714$

$S_2 = 5.714 / \sqrt{4} = 2.857$

t (calculated) = 5.0 / 2.857 = 1.750

t (3,0.025) = 3.182

Since the calculated value of "t" is less than tabulated, there is no significant change in suspended solids due to oxygenation.

For 50 mg O_3/L ozone dose.

$S_2 = 25.91$

$S = 5.089$

$S_d = 2.073$

t (calculated) = 5.5 / 2.073 = 2.653

t (3,0.025) = 3.183

No significant change in TSS due to 50 mgO_3/L dose.

For 100 O_3/L ozone dose

$S_2 = 52.23$

$S = 7.227$

$S_d = 2.940$

t (calculated) = 12.3 / 2.940 = 4.184

t (5,0.025) = 2.571

There is a significant reduction in TSS with 100 mg O_3/L dose.

APPENDIX X

SUMMERY OF COD, TOC AND SS FOR MILL EFFLUENTS

Table X.1 Chemical Oxygen Demand (mg/L) for Mill Effluents (Unfiltered)

Sample	Bleach effluent	Primary effluent	Secondary effluent			
			(Run 1&2)	(Run 3&4)	(Run 5)	(Run 6)
Raw sample	1169	694	448	566	524	451
Oxygen	1150	698	453	566	492	441
50 mg O3/L (Run1)	1092	678	454	520	446	441
50 mg O3/L (Run2)	1071	719	410	520	-	-
100 mg O3/L(Run1)	1059	621	415	498	451	437
100 mg O3/L(Run2)	1077	662	363	530	-	-
150 mg O3/L	-	-	-	-	385	391
200 mg O3/L	-	-	-	-	-	387

Table X.2 Chemical Oxygen Demand (mg/L) for Mill Effluents (Filtered)

Sample	Bleach Effluent	Primary Effluent	Secondary Effluent			
			(Run 1&2)	(Run 3&4)	(Run 5)	(Run 6)
Raw sample	986	651	367	478	406	367
Oxygen	1003	621	336	444	373	372
50 mg O3/L(Run1)	997	588	301	434	363	347
50 mg O3/L(Run2)	965	611	313	426	-	-
100 mg O3/L(Run1)	918	574	276	490	360	338
100 mg O3/L(Run2)	960	608	292	378	-	-
150 mg O3/l	-	-	-	-	296	309
200 mg O3/l	-	-	-	-	-	309

Table X.3 Total Organic Carbon (mg/L) for Mill Effluents (Unfiltered)

Sample	Bleach Effluent	Primary Effluent	Secondary Effluent			
			(Run 1&2)	(Run 3&4)	(Run 5)	(Run 6)
Raw sample	438	243	154	200	207	199
Oxygen	436	236	149	196	209	198
50 mg O3/L(Run1)	427	237	147	190	199	187
50 mg O3/L(Run2)	438	238	148	198	-	-
100 mg O3/L(Run1)	426	226	142	185	199	178
100 mg O3/L(Run2)	433	231	144	188	-	-
150 mg O3/L	-	-	-	-	191	168
200 mg O3/L	-	-	-	-	-	163

Table X.4 Dissolved Organic Carbon (mg/L) for Mill Effluents

Sample	Bleach Effluent	Primary Effluent	Secondary Effluent			
			(Run 1&2)	(Run 3&4)	(Run 5)	(Run 6)
Raw sample	429	218	136	149	161	145
Oxygen	431	211	131	146	152	143
50 mg O3/L(Run1)	431	218	125	133	140	136
50 mg O3/L(Run2)	432	222	127	135	-	-
100 mg O3/L(Run1)	413	217	125	135	145	131
100 mg O3/L(Run2)	409	218	128	134	-	-
150 mg O3/L	-	-	-	-	139	128
200 mg O3/L	-	-	-	-	-	127

Table X.5 COD/TOC for Mill Effluents (Unfiltered)

Sample	Bleach Effluent	Primary Effluent	Secondary Effluent			
			(Run 1&2)	(Run 3&4)	(Run 5)	(Run 6)
Raw sample	2.67	2.86	2.91	2.83	2.53	2.27
Oxygen	2.64	2.96	3.04	2.89	2.35	2.23
50 mg O3/L(Run1)	2.56	2.86	3.09	2.74	2.24	2.36
50 mg O3/L(Run2)	2.46	3.02	2.77	2.63	-	-
100 mg O3/L(Run1)	2.49	2.75	1.91	2.69	2.27	2.46
100 mg O3/L(Run2)	2.49	2.87	2.52	2.82	-	-
150 mg O3/L	-	-	-	-	2.02	2.33
200 mg O3/L	-	-	-	-		2.37

Table X.6 COD/TOC for Mill Effluents (Filtered)

Sample	Bleach effluent	Primary effluent	Secondary effluent			
			(Run 1&2)	(Run 3&4)	(Run 5)	(Run 6)
Raw sample	2.3	2.99	2.7	3.2	2.52	2.53
Oxygen	2.33	2.94	2.56	3.04	2.45	2.6
50 mg O3/L(Run1)	2.31	2.7	2.41	3.26	2.59	2.55
50 mg O3/L(Run2)	2.23	2.75	2.46	3.16	-	-
100 mg O3/L(Run1)	2.22	2.65	2.21	3.63	2.48	2.58
100 mg O3/L(Run2)	2.35	2.79	3.06	2.82	-	-
150 mg O3/L	-	-	-	-	2.13	2.41
200 mg O3/L	-	-	-	-	2.37	2.43

Table X.7 Total Suspended Solids (mg/L) for Mill Effluents

Sample	Bleach Effluent	Primary Effluent	Secondary Effluent			
			1 & 2	3 & 4	5	6
Raw sample	217	84	83	108	86	93
Oxygen	196	70	70	103	87	91
50 mg O3/L (Run#1)	182	71	80	99	98	93
50 mg O3/L (Run#2)	245	72	73	97	-	-
100 mg O3/L (Run#1)	205	63	63	90	82	89
100 mg O3/L (Run#2)	204	61	58	105	-	-
150 mg O3/L	-	-			79	79
200 mg O3/L	-	-			-	81

Table X.8 Volatile Suspended Solids (mg/L) for Mill Effluents

Sample	Bleach Effluent	Primary Effluent	Secondary Effluent			
			1 & 2	3 & 4	5	6
Raw sample	185	51	66	81	73	71
Oxygen	161	49	59	81	80	73
50 mg O3/L (Run#1)	147	51	66	80	83	74
50 mg O3/L (Run#2)	197	43	63	72	-	-
100 mg O3/L (Run#1)	153	48	54	69	73	72
100 mg O3/L (Run#2)	163	40	49	72	-	-
150 mg O3/L	-	-			63	64
200 mg O3/L	-	-			-	63